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 TRANSITION METAL HYDRIDO, AND
 TRIS (BENZENE-1,2-DITHIOLATO)
 COMPLEXES

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THE UNIVERSITY OF ALBERTA

STRUCTURAL DETERMINATIONS OF SOME TRANSITION
METAL HYDRIDO, AND *TRIS* (BENZENE-1,2-DITHIOLATO)
COMPLEXES

by



MARTIN COWIE

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled STRUCTURAL DETERMINATIONS OF SOME TRANSITION METAL HYDRIDO, AND *TRIS*(BENZENE-1,2-DITHIOLATO) COMPLEXES submitted by MARTIN COWIE in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

TO MY PARENTS

ABSTRACT

The crystal and molecular structures of $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ and $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ have been determined. The central Re_2Si_2 clusters are similar in both molecules and form a rhombus with a Re-Re bond across the shorter diagonal. The Re-Si bond lengths in both compounds are all similar, and are therefore consistent with the hydrogen ligands being terminally bound to the rhenium atoms rather than bridging the rhenium-silicon bonds. The mode of bonding of the hydride ligands is discussed in relation to other similar systems.

The crystal and molecular structures of three *tris* (benzene-1,2-dithiolato) complexes, $(\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3)_3$, $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3]$ and $[(\text{CH}_3)_4\text{N}]_2[\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3]$ have been determined in an attempt to explain the stability of the trigonal prism with respect to the octahedron. In the molybdenum and niobium complexes the metals are surrounded by six sulfur atoms in trigonal prismatic coordination. The zirconium complex, however, has a coordination which is best described as a distorted octahedron. The increase in S-C distances, observed through this series, indicates an increasing tendency of the ligands towards the reduced $\text{S}_2\text{C}_6\text{H}_4^{2-}$ formulation. This ten-

dency is discussed in relation to a molecular orbital scheme for trigonal prismatic dithiolenes (by Gray *et. al.*) and is correlated to the destabilization of the prism which is observed progressing through this series.

A disorder in $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$, involving a small translation of the complete molecule along the crystallographic *b* axis, was investigated in order to ascertain the effect on molecular geometry and thermal parameters.

PREFACE

This thesis presents the results of two independent problems. The first section deals with a structural study of a particular class of transition metal hydrides. The second section is concerned with the structures of transition metal complexes of ligands coordinated through sulfur atoms. The same technique, namely single crystal X-ray diffraction, was used for both problems. The theoretical and experimental details of X-ray diffraction are described in several standard reference texts.^{1,2,3,4}

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CHAPTER I: TRANSITION METAL HYDRIDE

INTRODUCTION

The discovery of the first transition metal hydride complexes,^{5,6} $\text{FeH}_2(\text{CO})_4$ and $\text{CoH}(\text{CO})_4$, in the 1930's marked the beginning of approximately twenty years of controversy concerning the structures of hydride complexes and the mode of bonding of the hydrogen atoms in these complexes.

The first electron diffraction study⁷ on gaseous $\text{CoH}(\text{CO})_4$ and $\text{FeH}_2(\text{CO})_4$ led to the conclusion that the metals were surrounded tetrahedrally by the carbonyl groups. The hydrogen atoms were assumed to be bound to the oxygen atoms of the carbonyl groups. Hieber later suggested⁸ that the hydrogens were actually bonded to the metals, but were buried in the electron density of the metal and thus had no stereochemical influence.

The infrared spectrum of $\text{CoH}(\text{CO})_4$ was initially interpreted⁹ as being consistent with the hydrogen atom being primarily bonded to the carbon p_π orbitals at approximately 2.0 \AA from the cobalt atom. In this model the hydrogen was believed to be bridging three carbonyl groups. However the findings of Cotton and Wilkinson,¹⁰ based on nuclear magnetic

resonance and acid dissociation constants for $\text{CoH}(\text{CO})_4$ and $\text{FeH}_2(\text{CO})_4$, agreed with Hieber,⁸ suggesting that the hydrogens were close to and primarily bonded to the metal atoms. Subsequent L.C.A.O. calculations¹¹ on $\text{CoH}(\text{CO})_4$ yielded the greatest total overlap integral of Co-H and C-H for a Co-H distance of 1.2 Å. This distance was again consistent with the hydrogen being buried in the Co orbitals, since a covalent distance of 1.593 Å had been obtained¹² in CoH.

Since $\text{HMn}(\text{CO})_5$ had physical properties¹³ similar to $\text{Fe}(\text{CO})_5$, its infrared spectrum was interpreted assuming it, like $\text{Fe}(\text{CO})_5$, had trigonal bipyramidal coordination,^{14,15} with the hydrogen buried in the manganese orbitals and exerting no stereochemical influence. In addition the identification¹⁶ of the Co-H stretching frequency at 1934 cm^{-1} added further proof that the hydrogen was bound to the metal. The large shifts to high field of the proton resonance that were observed in transition metal hydrides were also initially interpreted as evidence for "buried" hydrogens. However subsequent studies^{17,18} showed that these shifts were due to more subtle electronic effects and could be explained assuming normal metal-hydrogen covalent distances.

In addition it was shown¹⁹ that the neglect of quadrupole effects which resulted^{20,21} in short M-H distances, was not justified.

Thus until 1959 the experimental evidence was interpreted as indicating that the hydrogen atom exerted no stereochemical influence and was buried in the transition metal orbitals.

Discovery of the true coordination in the metal hydride complexes had to await the availability of good quality X-ray and neutron diffraction data and also the discovery of stable crystals of these hydrides [$\text{CoH}(\text{CO})_4$ and $\text{FeH}_2(\text{CO})_4$ were unstable gases]. In X-ray diffraction studies, since the X-rays are scattered by electrons, hydrogen atoms contribute little to the total scattering. Therefore location of the hydrogen atom requires extremely high quality data, and the difficulty of direct observation of hydrogen atoms increases with increasing atomic number of the atoms present. However, even when the hydrogen atom is not located, its approximate position can be deduced from the coordination of the other ligands. In neutron diffraction the scattering of thermal neutrons is by the nucleus and varies²² approximately as $A^{1/3}$ (where A is the atomic mass number). Thus the scattering amplitudes

of all atoms are of the same order of magnitude, allowing the hydrogen atoms to be located with a precision comparable to that of heavier atoms.

The X-ray structural determinations^{23,24} of $\text{PtHBr}[\text{P}(\text{C}_2\text{H}_5)_3]_2$ and $\text{OsHBr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ and later²⁵ of $\alpha\text{-HMn}(\text{CO})_5$ failed to locate the hydrogen atoms but showed the empty coordination sites where the hydrogens were probably located. In the X-ray crystallographic study²⁶ of $\text{RhH}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$, however, the hydrogen atom *was* located, at $1.72(15) \text{ \AA}$ from the rhodium atom, a distance consistent with the sum of the rhodium and hydrogen covalent radii.²⁷ (The reliability of this hydrogen identification has recently been challenged.²⁸ However the original paper²⁶ clearly outlined the conditions that would favour the direct observation of hydrogen atoms in heavy atom structures and provided the impetus for crystallographers to attempt hydrogen atom location.)

Neutron diffraction experiments^{29,30} on K_2ReH_9 and also $\beta\text{-HMn}(\text{CO})_5$ proved unequivocally that the hydrogens acted as typical ligands and were not buried in the metal orbitals. The Re-H distances average $1.68(1) \text{ \AA}$ and the Mn-H distance is $1.601(16) \text{ \AA}$ in these compounds.

It was a fortunate sequence of events that the molecular structure³¹ of $\text{RhH}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ was not determined prior to those mentioned above. Otherwise the hypothesis that the hydrogen was buried in the metal orbitals might have had a longer lifetime. In this compound the phosphorus atoms form, within experimental error, a regular tetrahedron about the Rh atom. Although it seems that the hydrogen is exerting no stereochemical influence, its influence is just minimized by the bulky $\text{P}(\text{C}_6\text{H}_5)_3$ groups. Comparing for example the volume^{32,33,34} of a $\text{P}(\text{C}_6\text{H}_5)_3$ group at $\sim 370 \text{ \AA}^3$ to that of CO ($\sim 45 \text{ \AA}^3$)³⁵ and H ($\sim 7 \text{ \AA}^3$)³⁶ it becomes obvious that this distortion is reasonable.

Of the many subsequent transition metal hydride complexes to be studied^{35,37,38} some of the most interesting involved bridging hydrogens, where the hydrogen ligands were simultaneously bonded to two atoms. Two main categories of bridging hydrogens exist, the most common being between two transition metals, and the second involving bridging between a transition metal and a non-transition metal. In the former category two types have been observed, involving either a bent or a linear M-H-M bond.

A linear M-H-M bond^{39,40} was deduced in the

structure of $\text{Cr}_2\text{H}(\text{CO})_{10}^-$. Although the hydrogen atom position was not located, stereochemical and bonding arguments suggest that it is collinear with the two chromium atoms and equidistant from each. [It is to be noted, however, that the X-ray data cannot differentiate between two possibilities: either the hydrogen is bonded symmetrically to both chromium atoms (single-minimum potential well), or it is preferentially bonded to one chromium atom (double-minimum potential well) and is "tunnelling" between the two sites.] The observed Cr...Cr distance of $3.41(1) \text{ \AA}$ is considerably longer than the Cr-Cr bond length³⁹ of $2.97(1) \text{ \AA}$ in $\text{Cr}_2(\text{CO})_{10}^{2-}$ and yields a Cr-H distance of 1.70 \AA which is in good agreement with the other known metal-hydrogen distances. The hydrogen ligand then occupies the sixth coordination site of each $\text{Cr}(\text{CO})_5$ fragment giving the anion D_{4h} symmetry. The insertion of the hydrogen ligand causing the two $\text{Cr}(\text{CO})_5$ moieties to be further apart also results in the carbonyl groups being eclipsed, compared with the staggered carbonyls in $\text{Cr}_2(\text{CO})_{10}^{2-}$. More recently a linear Re-H-Cr bond has also been inferred⁴¹ in $(\text{OC})_5\text{ReHCr}(\text{CO})_5$. Although the hydrogen was not located it was considered to be collinear with the Re and Cr atoms, since again the two metal-

pentacarbonyl groups are eclipsed and since the least squares planes containing the equatorial CO groups are within 2.5° of being parallel. The Re-Cr distance is $3.435(1) \text{ \AA}$, which is again consistent with hydrogen insertion between the two metals.

Bent M-H-M bonds have been deduced in several complexes. In $\text{Re}_3\text{H}(\text{CO})_{12}^{2-}$ and $\text{Re}_3\text{H}_2(\text{CO})_{12}^-$ the triangular species^{42,43} contain an isosceles triangle of rhenium atoms with Re-Re distances of $\sim 3.04 \text{ \AA}$ and 3.17 \AA , with the longer distances presumably being bridged by the hydrogen ligands. These bent hydrogen bridges were confirmed recently⁴⁴ in the analogous $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ complex, in which the hydrogen atoms were located. The manganese atoms form an equilateral triangle with the hydrogen ligands symmetrically bridging the triangle edges. The average Mn-Mn distance is 3.111 \AA compared with 2.923 \AA in $\text{Mn}_2(\text{CO})_{10}$ ⁴⁵ and thus again shows the lengthening of the bridged metal-metal bond, a feature which has been used as evidence for hydrogen bridging in the rhenium clusters.^{42,43} The average Mn-H distance is 1.72 \AA .

In $\text{Re}_2\text{MnH}(\text{CO})_{14}$ ^{46,47} and $\text{Re}_3\text{H}(\text{CO})_{14}$ ⁴⁸ the hydrogen ligands are located between the rhenium atoms in a position which is almost collinear with

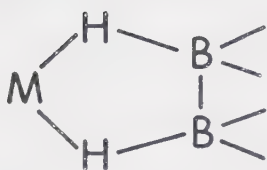
these atoms. However the estimated Re-H-Re angles, calculated assuming octahedral coordinations, are 164° in $\text{Re}_2\text{MnH}(\text{CO})_{14}$ and 159° in $\text{Re}_3\text{H}(\text{CO})_{14}$.

The structure⁴⁹ of $\text{Mo}_2\text{H}(\text{CO})_4(\pi\text{-C}_5\text{H}_5)_2[\text{P}(\text{CH}_3)_2]$ consists of two $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2$ fragments joined at the Mo atoms by a symmetrically bridged $\text{P}(\text{CH}_3)_2$ group and presumably by a hydrogen atom. The structure⁵⁰ of $\text{Mn}_2\text{H}(\text{CO})_8[\text{P}(\text{C}_6\text{H}_5)_2]$ closely resembles that of $\text{Mo}_2\text{H}(\text{CO})_4(\pi\text{-C}_5\text{H}_5)_2[\text{P}(\text{CH}_3)_2]$ with two carbonyl groups on each metal replacing a $(\pi\text{-C}_5\text{H}_5)$ group. However, in the manganese compound the hydrogen atom *was* located, in the position equivalent to that postulated in the molybdenum complex, with a Mn-H distance of $1.86(6) \text{ \AA}$ and a Mn-H-Mn angle of $104(5)^\circ$.

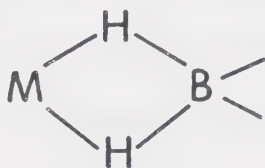
Hydrogen bridging three metal atoms has been postulated in $\text{Ru}_6\text{H}_2(\text{CO})_{18}$ ⁵¹ and $\text{Rh}_3\text{H}(\pi\text{-C}_5\text{H}_5)_4$ ^{52,53}. The ruthenium structure consists of an octahedron of Ru atoms each bound to three terminal carbonyl groups. The hydrogen ligands appear to occupy two opposite faces of the octahedron. In $\text{Rh}_3\text{H}(\pi\text{-C}_5\text{H}_5)_4$ the equilateral triangle of Rh atoms has one cyclopentadienyl ring bonded to each Rh with the fourth ring parallel to the rhodium triangle. The hydrogen ligand is then postulated as being equidistant from each Rh on the opposite side of the triangle from

the fourth C_5H_5 group.

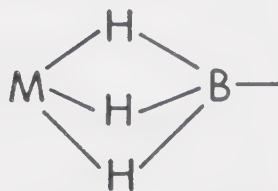
Hydrogen bridging between a transition metal and a non-transition metal has been observed in boron complexes with the hydrogen bridging the boron and the transition metal. Three basic types exist:



I



II



III

Structures of type I were observed in $Mn_3H(BH_3)_2(CO)_{10}$,⁵⁴ $Cu(B_3H_8)[P(C_6H_5)_3]_2$ ⁵⁵ and $Cr(B_3H_8)(CO)_4^-$.^{56,57,58}

In the manganese compound all hydrogen atoms of the BH_3 group are coordinated to a Mn atom and in addition a bent Mn-H-Mn bond exists between the two $Mn(CO)_3$ moieties. In $Cu(B_3H_8)[P(C_6H_5)_3]_2$ the coordination of the copper atom is a distorted tetrahedron with two of the coordination sites occupied by bridging hydrogens. The P-Cu-P and H-Cu-H angles of 120° and 103° respectively, reflect this distortion. $Cr(B_3H_8)(CO)_4^-$ has an octahedrally hybridized chromium atom with two sites again being occupied by bridging hydrogens.

Coordination of type II is exhibited^{59,60} by $\text{Cu}(\text{BH}_4)[\text{P}(\text{C}_6\text{H}_5)_3]_2$. The copper geometry again is distorted tetrahedral with two hydrogen atoms of the borohydride group bridging the copper and boron atoms. The short Cu-B distance of $2.184(9) \text{ \AA}$ and long Cu-H distance of $2.02(5) \text{ \AA}$ suggests delocalized bonding between the copper atom and the borohydride group in which direct Cu-B overlap might be significant.

In $\text{Zr}(\text{BH}_4)_4$ ⁶¹ the molecule is crystallographically required to possess T_d symmetry. The zirconium atom is tetrahedrally surrounded by the four boron atoms, and one terminal hydrogen atom is located on each C_3 axis. So it appears that M-H-B bonding of type III is present with the Zr atom surrounded by twelve H atoms.

The reactions of disubstituted silanes with dirhenium decacarbonyl and with both tungsten and molybdenum hexacarbonyls produced an interesting series of silicon-bridged, metal-metal bonded species which were also postulated as containing hydrogen-bridged metal-silicon bonds.^{62,63} Since this was only the second class of compounds in which hydrogen was postulated as bridging a transition metal-non-transition metal bond, a systematic study of the representative molecules from this series was therefore

undertaken to elucidate the major structural characteristics of the systems.

Viewing only the central cluster and ignoring the carbonyl groups, the molecules fall into five major classes:

- I. no hydrogen ligands,⁶⁴ e.g. $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$,
- II. two hydrogens, each on different transition metals but adjacent to the same silicon atom^{62,65}
e.g. $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$,
- III. two hydrogens, each on different transition metals and adjacent to two different silicon atoms,⁶⁶ e.g. $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$,
- IV. two hydrogens, both on the same transition metal but adjacent to different silicons, e.g.
 $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$, and
- V. four hydrogens, two attached to each transition metal, each silicon having two adjacent hydrogens,
e.g. $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$.

The structural fragments are shown in Fig. 1 using valence bond description and normal terminal transition metal hydride formulation, with the exceptions of III(b) where bridging hydrogens are indicated and III(c) where the terminal hydrogens interact weakly with the silicon atoms. The main interest in this series centred around the central cluster of transition

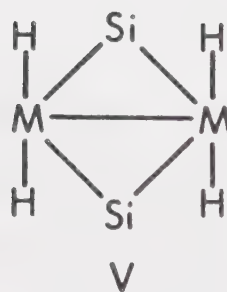
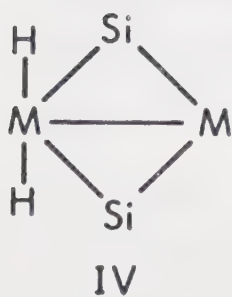
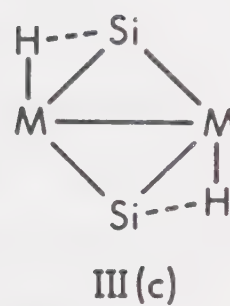
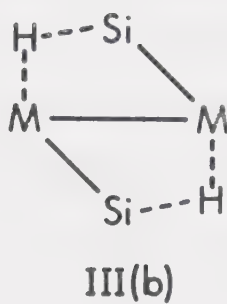
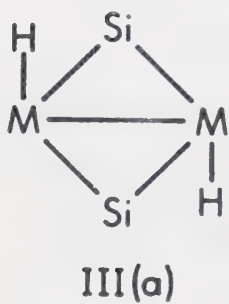
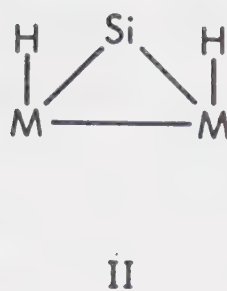
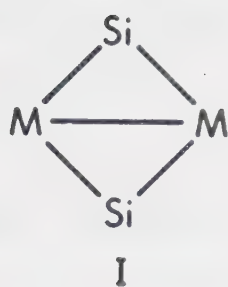


Fig. 1: CENTRAL FRAMEWORKS OF THE SILICON-BRIDGED
TRANSITION METAL SERIES.

metal and silicon atoms, especially when hydrogen ligands were present, to obtain information concerning the nature of the bonding of the hydrogen ligands.

It had been suggested on the basis of spectroscopic evidence that in these compounds the hydrogen ligands bridged the metal-silicon bonds rather than being bonded terminally to the metals.^{62,63} The basis of this argument was the spectroscopic studies by Kaesz and coworkers^{67,68} on the trimeric rhenium hydride $[\text{HRe}(\text{CO})_4]_3$ and its deuteride $[\text{DRe}(\text{CO})_4]_3$, in which the absence of a distinct metal-hydrogen stretching frequency in the infrared was interpreted as evidence that the hydrogens were bridging. Since the terminal metal-hydrogen stretch should be visible in the infrared, its silence was postulated as a characteristic feature of M-H-M bridges. This was extended to the series of transition metal silicon hydrides where the metal-hydrogen stretch was again absent in the infrared,⁶³ and consequently a Si-H-M bridge was postulated. In addition, in $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{CH}_3)_2$, the methyl resonance appeared as a 1:2:1 triplet at $\tau = 8.87$ with a coupling constant $J = 1.5 \text{ Hz}$.⁶³ The magnitude of this coupling constant also suggested that the high field protons, which are splitting the methyl resonance, were close to the dimethyl-silicon moiety since $J(\text{CH}_3\text{-Si-H}) = 4.2 \text{ Hz}$ for dimethyl-

silane alone.

The first member of this series to have its molecular structure solved by X-ray techniques was $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$.^{62,65} Unfortunately, due to the dominance of the rhenium scattering, location of the hydrogen ligands was not possible. However, the coordination sites adjacent to the metal-silicon bonds were conspicuously vacant so the approximate locations of the hydrogens were apparent. Elder postulated⁶⁵ that the hydrogens were located in the Re_2Si plane such that the Re-Re-H angle was 90° . Thus for a rhenium-hydrogen bond length²⁹ of 1.68 \AA , a silicon-hydrogen bond length of 1.59 \AA would result. This position he said would give the proper orientation for a three centre Si-H-Re bond.

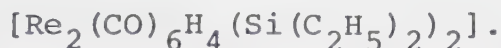
However, the subsequent structure determination of the non-hydridic species $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$ ⁶⁴ showed a remarkable similarity in Re-Si bond lengths [$2.542(3) \text{ \AA}$] with $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$, [$2.544(9) \text{ \AA}$], which was not expected if a three centre two electron Si-H-Re bond is involved in the latter. An unambiguous comparison of the two structures was hindered, however, by the realization that a disorder problem was present in $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$ (see Appendix 1). Although it was not believed that this

would affect the bond lengths in the central Re_2Si_2 cluster, it did cast some doubt on accurate comparisons of the two compounds.

Further evidence favouring the three centre Si-H-M bond arose from the structural determination of $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$,⁶⁶ [type III(b) in Fig. 1] in which two differing tungsten-silicon bonds were found [$2.586(5) \text{ \AA}$ and $2.703(4) \text{ \AA}$]. This was interpreted as being due to hydrogen insertion in the tungsten-silicon bond, thus forming a three centre W-H-Si bond. Therefore the crystal and molecular structure determinations of members IV and V ($\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ and $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$) were undertaken to obtain further information concerning the bonding of the hydrogen ligand in this series. These structure determinations are described in Chapters II and III.

CHAPTER II: THE CRYSTAL AND MOLECULAR STRUCTURE OF
DIHYDRIDO TRICARBONYL RHENIUM *BIS*

(μ -DIETHYLSILICON) DIHYDRIDO TRICARBONYL RHENIUM,



EXPERIMENTAL

The sample of $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ which was kindly supplied by Dr. Graham and Mr. Hoyano⁶³ was recrystallized from normal hexane, yielding colourless crystals with the shape of a general parallelepiped. Preliminary photography indicated only Laué symmetry $\bar{1}$ indicative of a triclinic space group. The systematic absences for the working cell, as determined by Weissenberg ($0k\ell$, $1k\ell$, $2k\ell$: CuK_{α} X-radiation), and Precession methods ($h0\ell$, $h1\ell$, $h2\ell$, $hk0$, hkl , $hk2$: MoK_{α} X-radiation), are hkl : $h + k = 2n + 1$, $h + \ell = 2n + 1$, $k + \ell = 2n + 1$, and are consistent with the non-standard space groups $F1$ and $F\bar{1}$. The non-standard cell was retained as the working cell for its convenience with respect to the crystal morphology and unit cell angles. Precise lattice parameters were obtained at 23°C from an analysis of the setting angles for 18 reflections which had been carefully centred on a Picker manual four circle diffractometer using CuK_{α_1} radiation of wavelength 1.54051 Å.

A Delaunay reduction was performed⁶⁹ and failed to show the presence of higher symmetry. The F centred cell parameters are : $a = 8.357(3) \text{ \AA}$, $b = 16.228(6) \text{ \AA}$, $c = 18.184(6) \text{ \AA}$, $\alpha = 118.98(2)^\circ$, $\beta = 92.62(3)^\circ$ and $\gamma = 95.44(3)^\circ$, and the reduced primitive cell parameters are: $a = 8.357(3) \text{ \AA}$, $b = 8.767(3) \text{ \AA}$, $c = 8.776(3) \text{ \AA}$, $\alpha = 109.07(3)^\circ$, $\beta = 97.76(3)^\circ$, and $\gamma = 112.88(3)^\circ$. The reduced primitive cell is related to the F centred cell by: $a_P = -a_F$, $b_P = 1/2(b_F + a_F)$, $c_P = -1/2(b_F + c_F)$. The observed density [$2.23(2) \text{ g cm}^{-3}$] obtained by floatation in aqueous Clerici's solution (Thallous formate-malonate, $\rho_{\text{max}} = 4.3 \text{ g ml}^{-1}$), is in satisfactory agreement with that calculated on the basis of four molecules in the F centred cell (2.25 g cm^{-3}). For space group $F\bar{1}$ the imposed symmetry on the molecule is $\bar{1}$, while no restrictions are possible for space group $F 1$. Since $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ can have $\bar{1}$ symmetry, $F\bar{1}$ was chosen and was later verified by successful refinement of the model. The General Equivalent Positions for the space group $F\bar{1}$ are : $\pm(x, y, z; 1/2 + x, 1/2 + y, z; 1/2 + x, y, 1/2 + z; x, 1/2 + y, 1/2 + z)$.

Intensity data were collected on the Picker manual diffractometer using CuK_α radiation monochromated by the (002) reflecting plane of an oriented graphite

crystal using a take-off angle of 2° . Two crystals were used during data collection and in each case they were aligned with their a^* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as: crystal 1 - $\{1,0,0\}$, 0.095 mm; $\{0,1,0\}$, 0.065 mm; $\{0,\bar{1},1\}$, 0.084 mm; and crystal 2 - $\{1,0,0\}$, 0.077 mm; $\{0,0,1\}$, 0.065 mm; and $\{0,\bar{1},1\}$, 0.036 mm. Data were collected for reflections with 2θ values between 0° and 125° using the coupled $\omega/2\theta$ scanning technique with a 2θ scan speed of $2^\circ/\text{min}$ and scan width of three degrees (to allow for increase in mosaic spread as crystal decomposition occurred). Stationary background counts were measured at the limits of each scan for 20 seconds. Assuming approximate linearity of background, the intensity of the peak (I) is given by:

$$I = P - t(B_1 + B_2) \quad (1)$$

where P = peak count, $t = t_p/t_B$ or the ratio of peak scan time to the sum of the background times, and B_1 and B_2 are the background counts. Standard deviations of the intensities were computed from the relationship:

$$\sigma(I) = (P + t^2 B + p^2 I^2)^{1/2} \quad (2)$$

where $B = B_1 + B_2$. An ignorance factor (p) of 0.03 was used to account for machine errors and to prevent unreasonably high weighting being applied to reflections of high intensity.⁷⁰ The detector was a scintillation counter and was used in conjunction with a pulse height analyzer which was tuned to accept 95% of the CuK_α peak.

Eight well distributed standard reflections were monitored at approximately 10 hour intervals to investigate possible decomposition. The decomposition was found to be approximately linear with time and was essentially free of $\sin \theta/\lambda$ dependence. The total decomposition for the data collection was about 10%. The 1690 unique reflections collected were reduced to 1510 using the criterion that a peak is significantly above background when $I/\sigma(I) \geq 3.0$. The significant data were reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. Standard deviations in the structure factors, $\sigma(F)$, were obtained from the expression:⁷¹

$$\sigma(F) = \frac{1}{2} \sqrt{\frac{D}{ALp'}} \cdot \frac{\sigma(I)}{I^{1/2}} \quad (3)$$

where D , A , L , and p' are the decomposition, absorption,⁷² Lorentz, and polarization correction factors res-

pectively. The high linear absorption coefficient⁸⁶ for $\text{Re}_2(\text{CO})_6\text{H}_6[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ using CuK_α X-radiation (226.07 cm^{-1}) gave rise to a wide range of transmission factors (0.138 to 0.382) which made an absorption correction imperative. The absorption correction was verified by observation of the variation in I_{h00} ($\chi = 90^\circ$) as ϕ was varied. The final corrected intensities of this ϕ scan data showed variation from the mean of less than 10% and thus were judged to be internally consistent.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson map^{73,74} was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, and $0 \leq w \leq 0.5$. The Re-Re, Re-Si, and Si-Si vectors are derived for space group $P\bar{1}$ in Table 1. The vectors for space group $F\bar{1}$ are generated by adding $(0,0,0)$, $(1/2,1/2,0)$, $(1/2,0,1/2)$ and $(0,1/2,1/2)$ to those derived for $P\bar{1}$. In addition all vector multiplicities increase by a factor of 4. The origin peak is due to the sum of the vectors between every atom and itself, thus the magnitude of the origin vector is roughly given by: $(2 \times 75^2 + 2 \times 14^2 + 6 \times 8^2 + 14 \times 6^2 + 24 \times 1^2) = 12554$. In the Fourier

program used to calculate the vector map, however, the origin peak is normalized to 1000. Therefore taking account of the largest negative peak (~ -40), and assuming the temperature factors are comparable, one expects the Re-Re vectors to have approximate magnitude 466, the Re-Si vectors ~ 174 and the Si-Si vectors ~ 17 above background. Viewing the Patterson map (summarized in Table 2) it is obvious that the first two vectors correspond to Re-Re vectors. On inspection of the map the first vector is identified as associated with the $0, 1/2, 1/2$ origin therefore is attributed as $(2x_R, 1/2 + 2y_R, 1/2 + 2z_R)$. The coordinates of the rhenium atom are then calculated as $(0.120, -0.010, -0.061)$. The second peak then corresponds to the edge of the vector $(1/2, 1/2, 0) - (2x_R, 2y_R, 2z_R)$.

The next most intense peak, having a magnitude approximately comparable to that expected for a Re-Si vector, was situated at approximately 2.44 \AA from the origin (a distance which is similar to the Re-Si distance in $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2^{62,65}$). For this reason it was chosen as the $(x_R - x_S, y_R - y_S, z_R - z_S)$ vector and from this the silicon coordinates were calculated as $(-0.08, -0.13, -0.61)$. The next two vectors were then identified as $(1/2, 1/2, 0) - (x_R - x_S,$

TABLE 1: DERIVATION OF Re-Re, Re-Si, AND Si-Si VECTORS FOR SPACE GROUP $P\bar{1}$

	x_R', y_R', z_R' ^a	$-x_R', -y_R', -z_R'$	x_S', y_S', z_S'	$-x_S', -y_S', -z_S'$
x_R', y_R', z_R'	$0, 0, 0$	$-2x_R', -2y_R', -2z_R'$	$-(x_R' - x_S'),$ $-(y_R' - y_S'),$ $-(z_R' - z_S')$	$-(x_R' + x_S'),$ $-(y_R' + y_S'),$ $-(z_R' + z_S')$
$-x_R', -y_R', -z_R'$	$2x_R', 2y_R', 2z_R'$	$0, 0, 0$	$x_R' + x_S',$ $y_R' + y_S',$ $z_R' + z_S'$	$x_R' - x_S',$ $y_R' - y_S',$ $z_R' - z_S'$
x_S', y_S', z_S'	$x_R' - x_S',$ $y_R' - y_S',$ $z_R' - z_S'$	$-(x_R' + x_S'),$ $-(y_R' + y_S'),$ $-(z_R' + z_S')$	$0, 0, 0$	$-2x_S', -2y_S', -2z_S'$
$-x_S', -y_S', -z_S'$	$x_R' + x_S',$ $y_R' + y_S',$ $z_R' + z_S'$	$-(x_R' - x_S'),$ $-(y_R' - y_S'),$ $-(z_R' - z_S')$	$2x_S', 2y_S', 2z_S'$	$0, 0, 0$

^a (x_R', y_R', z_R') and (x_S', y_S', z_S') are the coordinates for the rhenium and silicon atoms respectively.

TABLE 2: ASSIGNMENT OF MOST INTENSE
PATTERSON VECTORS

u	v	w	RELATIVE PEAK HEIGHT	ASSIGNMENT
0.240	0.480	0.378	487	$(0, 1/2, 1/2) + (2x_R, 2y_R, 2z_R)$
0.240	~0.500	0.126	370	$(1/2, 1/2, 0) - (2x_R, 2y_R, 2z_R)^b$
0.200	0.120	0.0	131	$(x_R - x_S, y_R - y_S, z_R - z_S)$
0.280	0.380	0.0	123	$(1/2, 1/2, 0) - (x_R - x_S, y_R - y_S, z_R - z_S)$
0.040	0.360	0.360	119	$(0, 1/2, 1/2) + (x_R + x_S, y_R + y_S, z_R + z_S)$
0.240	0.040	0.396	98	Re-C and Re-O vector build-up.
0.480	0.460	0.234	91	
0.0	0.140	0.126	90	$-(x_R + x_S, y_R + y_S, z_R + z_S)^b$

^bshoulder of the peak.

$y_R - y_S, z_R - z_S$) and $(0, 1/2, 1/2) + (x_R + x_S, y_R + y_S, z_R + z_S)$. Image seeking around the Re-Re vectors then identified three of the next four vectors as being due to build-ups of Re-C and Re-O vectors from the molecules at $(1/2, 1/2, 0)$ and $(0, 1/2, 1/2)$. The peak observed at $\sim (0.00, 0.140, 0.126)$ was identified as the edge of the vector $-(x_R + x_S, y_R + y_S, z_R + z_S)$.

At this point it was obvious that the Re_2Si_2 core had an inversion centre or at least was very close to having one, otherwise a more complex vector pattern would have been expected corresponding to independent Re(1), Re(2), Si(1), and Si(2) positions.

A least squares refinement phased on the rhenium and silicon positions converged in two cycles yielding a discrepancy index, $R_1 = 0.132$, and a weighted residual, $R_2 = 0.186$. These "R factors" as calculated in the least squares program are defined as:

$$R_1 = \sum \left| |F_O| - |F_C| \right| / \sum |F_O| \quad (4)$$

$$R_2 = \left\{ \sum w(|F_O| - |F_C|)^2 / \sum w|F_O|^2 \right\}^{1/2} \quad (5)$$

where $|F_O|$ and $|F_C|$ are the observed and calculated structure factor amplitudes respectively, and w the weighting factor is defined by $w = 1/\sigma^2(F)$.

Structure factors were calculated using the atomic scattering factors⁷⁵ for rhenium and silicon atoms to which the anomalous dispersion corrections,⁷⁶ both real and imaginary were applied⁷⁷ ($\Delta f'_{\text{Re}} = -5.58$, $\Delta f''_{\text{Re}} = 5.37$, $\Delta f'_{\text{Si}} = 0.23$, $\Delta f''_{\text{Si}} = 0.36$). The function which was minimized during the least squares refinement was $\sum w(|F_o| - |F_c|)^2$.

An electron density difference map, phased on the rhenium and silicon atom positions, yielded the location of all other non-hydrogen atoms. A least squares calculation performed on all non-hydrogen atoms converged in two cycles to $R_1 = 0.061$ and $R_2 = 0.074$. Decomposition and absorption corrections were applied to the data and one further cycle of refinement gave $R_1 = 0.055$ and $R_2 = 0.073$. Comparison of $|F_o|$ and $|F_c|$ showed no indication of extinction problems so no correction was applied. This was reasonable considering the width of the peaks ($\sim 2^\circ$) indicating high mosaicity of the crystals.

Refinement of the model with rhenium and silicon atoms having anisotropic temperature factors gave $R_1 = 0.039$ and $R_2 = 0.053$ after two cycles. An electron density difference map phased on this model showed features in the regions of the other atoms which suggested that they too be given anisotropic temperature

factors. This gave $R_1 = 0.034$ and $R_2 = 0.045$ after a further two cycles of refinement. The form of the temperature factors used was:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

The validity of the anisotropic refinement was verified by a Hamilton's R test⁷⁹ at the 0.005 significance level.

An electron density difference map was calculated in an attempt to locate the hydrogen atoms in the structure, especially those attached to the rhenium atoms. It was encouraging that the highest peaks in the electron density difference map ($1.75 - 1.14 \text{ e } \text{\AA}^{-3}$) were located in the space between the rhenium and silicon atoms in the approximate position expected for a hydrogen bound to rhenium. For this reason the method of La Placa and Ibers³³ was used in an attempt to discern whether these peaks were hydrogen atoms or just artifacts arising from the improper treatment of the rhenium scattering or vibrations. Ibers reasoned that if the peak is not due to hydrogen scattering, then as the number of terms in the Fourier series is varied, the peak should disappear or shift markedly. A peak due to a hydrogen atom, however, should remain approximately in the same position and the peak height would be expected to vary in accordance

with the equation

$$\rho_H = \frac{1}{2\pi^2} \int_0^{s_0} (1 + a^2 s^2/4)^{-2} \exp(-Bs^2/16\pi^2) s^2 ds \quad (6)$$

where ρ_H is the electron density of the hydrogen atom, a is the Bohr radius = 0.5292 \AA , $s = 4\pi\lambda^{-1} \sin \theta$, and B is the hydrogen temperature factor. Using a temperature factor of 3.6, electron density difference maps were calculated for $\sin \theta/\lambda$ cut-offs of 0.2, 0.25, 0.3, 0.35, 0.4, 0.58 (Complete Data). The results are summarized in Table 3.

TABLE 3: OBSERVED AND CALCULATED ELECTRON DENSITIES
FOR VARYING $\sin \theta/\lambda$ CUT-OFFS

SIN θ/λ LIMIT	NUMBER OF TERMS	$\rho_{\text{CAL.}}$ (e\AA^{-3})	$\rho_{\text{OBS.}}$ (e\AA^{-3})
0.20	74	0.16	0.49 - 0.42
0.25	143	0.25	0.78 - 0.69
0.30	243	0.33	1.07 - 0.87
0.35	371	0.41	1.25 - 0.97
0.40	556	0.47	1.44 - 1.02
0.58 (Complete Data)	1509	0.63	1.75 - 1.14

The electron density observed is in all cases much greater than that calculated by Ibers' formula. A representation of the electron density difference

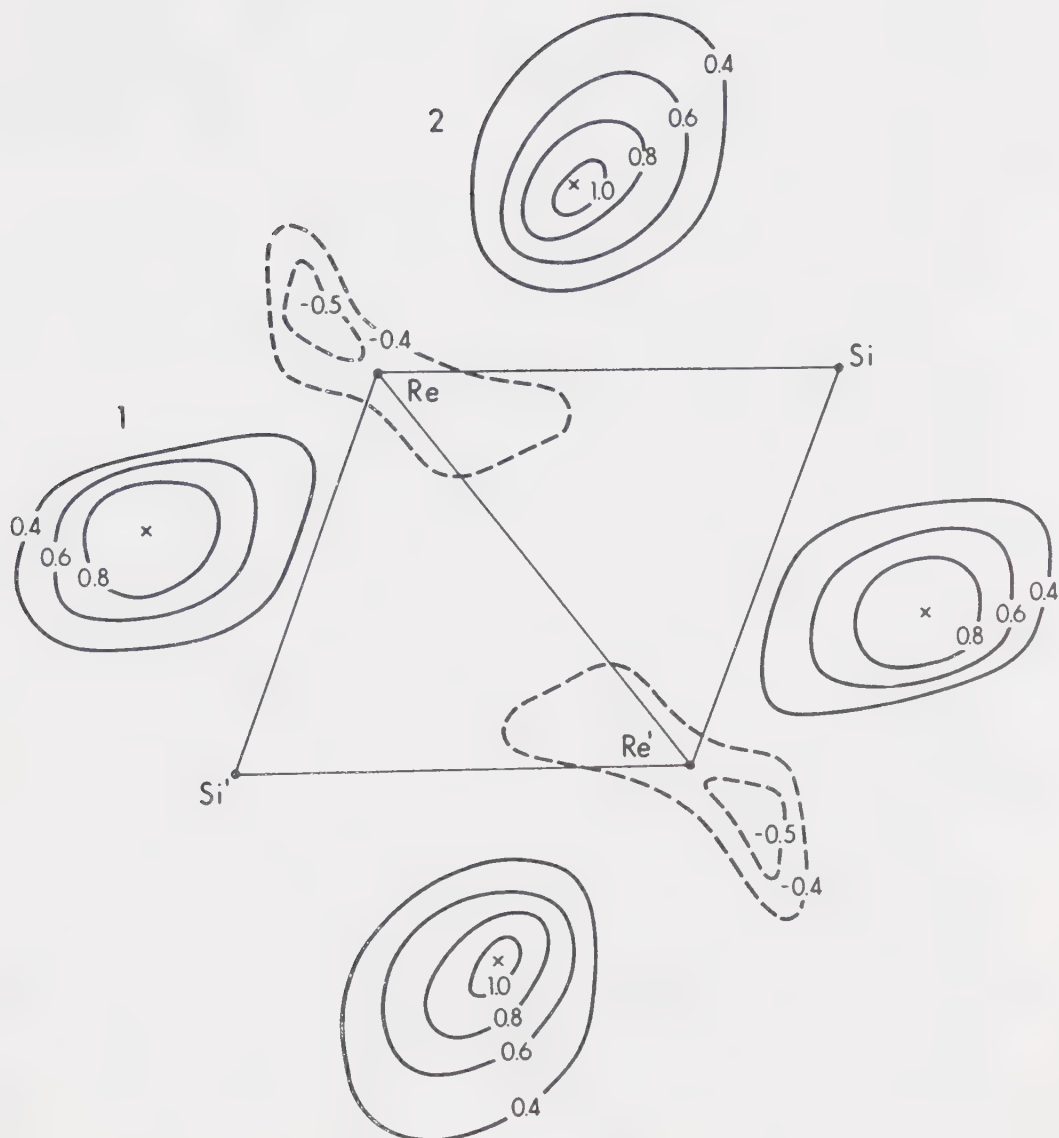


Fig. 2: ELECTRON DENSITY DIFFERENCE MAP THROUGH
THE Re_2Si_2 PLANE [$(\sin \theta/\lambda)_{\text{MAX}} = 0.35$].

map calculated through the plane of the rhenium and silicon atoms for a $\sin \theta/\lambda$ limit of 0.35 is shown in Figure 2. The hydrogen, which could be situated anywhere within the $0.4e \text{ \AA}^{-3}$ contour on this diagram, therefore cannot be located with certainty. This implied that the peak height, although being contributed to by the hydrogen, could be receiving a strong contribution due to the inadequacy in description of the rhenium scattering. For this reason several least squares refinements and corresponding electron density difference maps were calculated making changes of $\pm 0.5 e$ to each of the real and imaginary parts of the anomalous dispersion corrections in turn. This produced no changes in the refinements or in the difference maps. It was therefore concluded that the peaks, although possibly containing contributions due to the hydrogen atoms, are due mainly to inadequacies of the model or systematic errors in the data. Among these are inadequate description of the scattering due to the rhenium atoms and residual absorption effects. In addition, doubt concerning the degree of contribution of the hydrogen ligands to these peaks existed because of the failure to locate the methylene hydrogen atoms of the ethyl groups.

The computer programmes used in solution and

refinement of structure and presentation of Data are listed and briefly described in Appendix 2.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 4. The final fractional coordinates of all atoms except hydrogens are shown in Table 5, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic U's⁸⁰ and the equivalent isotropic B's⁸¹ of all atoms are shown in Table 6. Relevant bond lengths and bond angles are shown in Table 7. The bond lengths and angles along with their standard deviations were obtained from ORFFE. A packing diagram for the face centred cell, viewed onto the $0kl$ plane is shown in Figure 4. The open bonds indicate molecules in the $0kl$ plane whereas solid bonds indicate molecules in the $1/2 kl$ plane.

TABLE 4: OBSERVED AND CALCULATED STRUCTURE
FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	
3	15	670	660	10	-4	1724	1780	-5	-5	3897	3886	7	1	4726	4657	-10	18	943	936	
5	11	1151	1111	10	-2	2559	2624	-5	-3	1870	1991	7	3	1579	1527	-10	20	1315	1332	
5	13	1194	1156	10	0	1572	1469	-5	1	1048	1220	7	5	788	777	-8	-12	757	870	
7	11	1130	1069	10	2	276	318	-5	3	4308	4419	7	7	1838	1735	-8	-10	1283	1340	
7	13	1085	1118	10	4	1658	1594	-5	5	3258	2929	7	9	1717	1672	-8	-8	732	725	
9	7	1145	1135	10	6	1636	1587	-5	7	865	816	7	11	609	616	-8	-6	677	729	
9	9	671	620	12	-16	1190	1253	-5	9	2566	2487	9	-17	1322	1341	-8	-4	1858	1828	
9	11	1159	1195	12	-14	573	574	-5	11	2706	2623	9	-15	2029	2061	-8	-2	1795	1826	
11	3	1715	1604	12	-12	1046	988	-5	13	1355	1366	9	-13	1395	1395	-8	0	575	559	
11	5	1439	1351	12	-10	2052	1939	-5	15	526	506	9	-11	545	467	-8	2	1092	1095	
13	1	542	490	12	-8	1597	1478	-5	17	1560	1500	9	-9	2892	2872	-8	4	2642	2725	
13	3	1100	998	12	-6	503	408	-5	19	1137	1133	9	-7	2953	2946	-8	6	2240	2344	
13	5	850	840	12	-4	1105	1070	-3	-13	1818	1747	9	-5	677	651	-8	8	1598	1591	
15	-3	1374	1315	12	-2	1744	1750	-3	-11	1690	1617	9	-3	583	631	-8	10	2210	2085	
15	-1	360	365	12	0	1086	1038	-3	-9	2212	2242	9	-1	2349	2413	-8	12	1285	1230	
15	1	360	396	12	4	816	796	-3	-7	4397	4512	9	1	2858	2750	-8	14	327	195	
17	-5	1291	1326	12	6	1110	1149	-3	-5	3350	3423	9	3	665	639	-8	16	780	786	
17	-3	1017	1015	12	8	1110	1149	-3	-3	1616	564	9	5	899	850	-8	18	1070	1095	
-12	18	947	994	14	-18	982	1038	-3	-1	3449	3517	9	7	1289	1256	-6	-12	870	886	
-12	20	429	425	14	-16	1214	1245	-3	1	5258	4857	9	9	936	962	-6	-10	1764	1781	
-10	16	1881	1840	14	-14	418	359	-3	3	1253	1378	11	-17	874	928	-6	-8	1339	1346	
-10	18	1477	1476	14	-12	1078	1055	-3	5	1074	1080	11	-15	1872	1877	-6	-6	728	693	
-10	20	474	501	14	-10	1805	1750	-3	7	3026	2978	11	-13	1147	1137	-6	-4	2284	2342	
-8	12	829	822	14	-8	1542	1463	-3	9	11374	3212	11	-11	1541	1503	-6	-2	2190	2225	
-8	14	1676	1595	14	-6	452	395	-3	11	1085	1112	11	-9	2249	2117	-6	0	1367	1474	
-8	16	2740	2586	14	-4	1204	1218	-3	13	1161	1188	11	-7	1338	1368	-6	2	573	668	
-8	18	1366	1363	14	-2	1698	1719	-3	15	1800	1763	11	-5	1704	1683	-6	4	3986	4112	
-6	10	2705	2542	14	0	926	906	-3	17	992	1030	11	-3	1852	1795	-6	6	3443	3288	
-6	12	1782	1659	14	2	777	820	-3	19	1407	1382	11	-1	3	815	718	-6	8	796	721
-6	14	2131	2002	16	-16	903	932	-1	-13	2821	2659	11	1	307	332	-6	10	1409	1375	
-6	16	962	909	16	-14	1078	1118	-1	-11	1657	1660	11	3	950	950	-6	12	2937	2789	
-4	6	1811	1646	16	-12	1078	1118	-1	-9	902	812	13	-17	1137	1150	-6	14	2020	1907	
-4	8	3954	3857	16	-10	1842	1751	-1	-7	3556	3521	13	-15	1851	1891	-6	16	353	353	
-4	10	2524	2467	16	-8	1070	1033	-1	-5	5726	5777	13	-13	1174	1250	-6	18	815	803	
-4	12	267	260	16	-6	1157	1181	-1	-3	3190	3193	13	-11	2105	2011	-6	20	438	269	
-4	14	1393	1370	16	-4	1224	1249	-1	-1	2204	2152	13	-9	2308	2227	-6	22	1660	1633	
-4	16	2076	1959	16	-2	345	328	-1	1	6243	5578	13	-7	989	940	-6	24	2418	2344	
-2	4	1506	1456	16	0	881	536	-1	3	4097	4268	13	-5	527	508	-6	26	1041	1080	
-2	6	1799	1736	16	2	724	576	-1	5	1026	958	13	-3	1679	1689	-6	28	1321	1309	
-2	8	4109	4301	16	4	369	403	-1	7	2231	2362	13	-1	1655	1678	-6	30	3428	3621	
-2	10	2456	2473	16	6	327	367	-1	9	3968	4123	13	1	439	457	-6	32	3058	3388	
-2	12	1580	1547	18	-18	1214	1245	-1	11	2428	2469	13	3	640	694	-6	34	763	825	
-2	14	2068	1985	18	-16	1214	1245	-1	13	1389	1380	13	5	1116	1152	-6	36	2964	3015	
-2	16	924	925	18	-14	755	611	-1	15	1666	1671	13	7	1116	1152	-6	38	5707	5470	
0	4	1623	1535	18	-12	1078	1118	1	-17	585	533	15	-15	1572	1588	-6	40	3145	2956	
0	6	2199	2485	18	-10	1842	1751	1	-15	1884	1728	15	-13	693	677	-6	42	8	277	278
0	8	3853	4072	18	-8	1542	1463	1	-13	2332	2212	15	-11	799	850	-6	44	2208	2295	
0	10	2149	2206	18	-6	1157	1181	1	-11	812	813	15	-9	1806	1738	-6	46	123411	3462	
0	12	830	836	18	-4	1204	1218	1	-9	1358	1350	15	-7	1420	1392	-6	48	14606	1571	
0	14	2345	2256	18	-2	345	328	1	-7	3468	3464	15	-5	323	337	-6	50	18138	1137	
0	16	1729	1710	18	0	926	906	1	-5	3708	3426	15	-3	864	813	-6	52	466	406	
0	18	431	484	18	2	777	820	1	-3	2894	2838	15	-1	792	848	-6	54	891	854	
2	-2	556	4596	18	4	1204	1218	1	-1	4241	4703	17	-15	936	960	-2	-12	2174	2122	
2	0	5623	6229	18	6	1698	1719	1	1	2415	2477	17	-13	824	809	-2	-10	2478	2430	
2	2	2028	2023	18	8	1542	1463	1	3	527	487	17	-11	1140	1132	-2	-8	812	762	
2	4	871	925	18	10	1626	1542	1	5	2206	2345	17	-9	806	788	-2	-6	3210	3130	
2	6	2706	2833	18	12	1626	1542	1	7	2685	2754	17	-7	806	788	-2	-4	5651	5688	
2	8	2526	2684	18	14	1626	1542	1	9	11355	1345	17	-5	1137	1139	-2	-2	1885	1968	
2	10	457	420	18	16	1626	1542	1	11	1163	1126	18	-18	784	729	-2	0	2466	2376	
2	12	1024	1039	18	18	1626	1542	1	13	1126	1168	18	-16	721	712	-2	2	6142	6327	
2	14	1485	1461	18	20	1626	1542	1	15	1163	1126	18	-14	621	613	-2	4	2804	2863	
2	16	1083	1050	18	22	1626	1542	1	17	1163	1126	18	-12	708	704	-2	6	1164	1215	
4	-4	671	396	18	24	1626	1542	1	19	1163	1126	18	-10	621	613	-2	8	2480	2530	
4	-2	2760	2807	18	26	1626	1542	1	21	1163	1126	18	-8	621	613	-2	10	2437	2469	
4	0	5741	5656	18	28	1626	1542	1	23	1163	1126	18	-6	621	613	-2	12	989	1012	
4	2	1926	1914	18	30	1626	1542	1	25	1163	1126	18	-4	621	613	-2	14	502	513	
4	4	1136	1214	18	32	1626	1542	1	27	1163	1126	18	-2	621	613	-2	16	1087	1154	
4	6	2148	2086	18	34	1626	1542	1	29	1163	1126	18	0	621	613	-2	18	857	916	
4	8	1945	1961	18	36	1626	1542	1	31	1163	1126	18	2	621	613	-2	20	1150	1175	
4	10	897	956	18	38	1626	1542	1	33	1163	1126	18	4	621	613	-2	22	2178	2141	
4	12	582	570	18	40	1626	1542	1	35	1163	1126	18	6	621	613	-2	24	1342	1370	
4	14	1331	1320	18	42	1626	1542	1	37	1163	1126	18	8	621	613	-2	26	612	521	
4	16	3827	3795	18	44	1626	1542	1	39	1163	1126	18	10	621	613	-2	28	3120	3142	
4	18	6193	6021	18	46	1626	1542	1	41	1163	1126	18	12	621	613	-2	30	5197	5148	
4	20	2599	2917	18	48	1626	1542	1	43	1163	1126	18	14	621	613	-2	32	2340	2051	
4	22	4153	4040	18	50	1626	1542	1	45	1163	1126	18	16	621	613	-2	34	721	671	
4	24	1507	1449	18	52	1626	1542	1	47	1163	1126	18	18	621	613	-2	36</			

Table 4 (continued)

K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL
2	12	1817	1843	-15	7	1409	1301	-1	11	1356	1327	15	-11	1121	1117	-2	2	2191	2082
2	14	727	756	-15	9	1257	1216	-1	13	1742	1757	15	-7	613	577	-2	4	278	229
2	16	360	379	-15	11	464	485	-1	15	933	939	15	-5	944	966	-2	6	2128	2177
4	-18	1270	1249	-15	13	483	497	1	-17	1340	1308	15	-3	769	828	-2	8	3114	3125
4	-18	1880	1850	-15	15	1251	1307	1	-15	837	838	17	-11	990	943	-2	10	1149	1186
4	-12	3348	3206	-13	-5	477	520	1	-11	1928	1874	17	-9	301	250	-2	12	297	279
4	-10	1914	1815	-13	-3	600	517	1	-9	3451	3282	17	-7	400	350	-2	14	889	903
4	-8	367	275	-13	-1	1478	1502	1	-7	2127	2022	16	2	935	982	-2	16	1161	1168
4	-6	3781	3909	-13	1	1524	1555	1	-5	1034	1050	16	4	922	892	0	-16	1351	1352
4	-4	6094	6304	-13	3	593	554	1	-3	3406	3290	16	8	833	711	0	-14	1330	1318
4	-2	2325	2633	-13	5	1057	1017	1	-1	2578	2597	16	10	1300	1261	0	-10	1302	1287
4	0	1190	1158	-13	7	2299	2180	1	1	1383	1458	16	12	830	881	0	-8	3160	3067
4	2	3488	3611	-13	9	1580	1526	1	3	1133	1226	14	0	1123	1139	0	-6	2497	2416
4	4	3472	3500	-13	11	1111	1134	1	5	3871	3914	14	2	1545	1561	0	-4	322	223
4	6	927	929	-13	13	1663	1662	1	7	2598	2593	14	4	843	775	0	-2	2906	2714
4	8	1383	1342	-13	15	968	990	1	9	267	314	14	6	352	328	0	0	3966	4226
4	10	2212	2229	-11	-7	939	982	1	11	1275	1268	14	8	1256	1178	0	2	2154	2146
4	12	1633	1650	-11	-5	316	301	1	13	1749	1771	14	10	1644	1548	0	4	2461	2446
4	14	294	312	-11	-3	999	982	1	15	1075	1098	14	12	655	676	0	6	2974	3018
6	-20	1484	1533	-11	-1	2133	2161	3	-19	1237	1286	14	14	607	667	0	10	1172	1155
6	-18	872	871	-11	1	1667	1610	3	-17	1778	1785	14	16	1046	1108	0	12	555	543
6	-16	451	472	-11	3	1646	1670	3	-15	753	731	12	-6	975	1035	0	14	1271	1282
6	-14	2214	2080	-11	5	2582	2603	3	-13	975	963	12	-4	649	662	2	-18	896	918
6	-12	3141	3163	-11	7	1372	1417	3	-11	2888	2800	12	-2	537	419	2	-16	1652	1692
6	-10	1377	1430	-11	9	323	326	3	-9	3613	3431	12	0	1327	1316	2	-14	1242	1285
6	-8	1410	1425	-11	11	1273	1260	3	-7	1282	1182	12	2	1646	1621	2	-10	2732	2656
6	-6	3701	3682	-11	13	1550	1575	3	-5	3080	2965	12	4	794	834	2	-8	4643	4411
6	-4	3485	3654	-11	15	774	797	3	-3	4943	5057	12	6	577	604	2	-6	1742	1721
6	-2	1115	1202	-11	17	255	321	3	-1	2310	2758	12	8	1427	1426	2	-4	1093	1090
6	0	1736	1692	-9	19	1109	1097	3	1	252	213	12	10	1142	1219	2	-2	2986	3104
6	2	3608	3386	-9	21	996	1065	3	3	2755	2848	12	12	373	338	2	0	3853	4116
6	4	2067	2026	-9	23	1311	1322	3	5	3971	4053	12	14	645	683	2	2	1557	1659
6	6	1305	1278	-9	25	1900	1942	3	7	1799	1817	12	16	1126	1127	2	4	1359	1369
6	8	1622	1611	-9	27	1238	1275	3	9	411	338	12	18	757	784	2	6	2948	2991
6	10	891	924	-9	29	1757	1730	3	11	1722	1697	10	-8	674	678	2	8	2355	2334
6	12	1205	1238	-9	31	948	902	3	13	1723	1761	10	-6	1140	1156	2	10	375	391
6	14	444	482	-9	33	395	416	5	-19	1427	1440	10	-4	767	745	2	12	1005	995
6	16	1982	2050	-9	35	948	902	5	-17	1295	1292	10	-2	486	453	2	14	1280	1250
6	18	2406	2400	-9	37	1378	1364	5	-15	1262	1213	10	0	1495	1537	4	-18	1049	1050
6	20	443	508	-9	39	761	782	5	-13	2820	2782	10	2	1822	1844	4	-16	1629	1591
6	22	1399	1381	-9	41	386	347	5	-11	2075	2074	10	4	828	853	4	-14	580	600
6	24	2469	2478	-9	43	707	606	5	-9	717	570	10	6	640	639	4	-12	894	894
6	26	2230	2296	-7	-9	1685	1622	5	-7	3477	3740	10	8	1491	1502	4	-10	2536	2442
6	28	554	507	-7	-7	1519	1479	5	-5	3477	3740	10	10	1354	1385	4	-8	3111	3080
6	30	1762	1777	-7	-5	516	504	5	-3	1493	1482	10	12	527	491	4	-6	1061	1100
6	32	2504	2440	-7	-3	1137	1161	5	-1	423	397	10	14	785	798	4	-4	1228	1225
6	34	1281	1235	-7	-1	3225	3396	5	1	2386	2360	10	16	1377	1345	4	-2	2653	2834
6	36	888	871	-7	1	2336	2531	5	3	2636	2587	10	18	857	867	4	0	2160	2167
6	38	1049	1100	-7	3	1937	1956	5	5	732	730	8	-8	986	1011	4	2	261	194
6	40	1026	1112	-7	5	3509	3453	5	7	674	657	8	-6	1737	1673	4	4	1191	1175
6	42	639	668	-7	7	2187	2216	5	9	1207	1240	8	-4	1257	1273	4	6	2077	2010
6	44	472	458	-7	9	1592	1560	5	11	1280	1307	8	-2	505	449	4	8	1395	1406
6	46	1659	1643	-7	11	1766	1724	5	13	1215	1199	8	0	2212	2328	4	10	732	798
6	48	1843	1881	-7	13	854	809	5	15	1405	1417	8	2	2463	2557	6	-18	1056	1058
6	50	854	915	-7	15	373	388	5	17	2052	2035	8	4	1125	1165	6	-16	1499	1470
6	52	744	694	-5	-11	1246	1257	5	19	1232	1279	8	6	959	950	6	-14	549	605
6	54	2081	2076	-5	-9	2607	2677	5	21	2589	2607	8	8	2533	2522	6	-12	464	347
6	56	1926	1916	-5	-7	1978	1917	5	23	3454	3601	8	10	1994	1953	6	-10	1884	1988
6	58	623	642	-5	-5	410	431	5	25	1130	1231	8	12	424	409	6	-8	2949	3082
6	60	1222	1207	-5	-3	2569	2770	5	27	1502	1445	8	14	1047	1030	6	-6	1272	1233
6	62	2100	2069	-5	-1	3778	4085	5	29	1872	1846	8	16	1692	1658	6	-4	1053	1051
6	64	1290	1270	-5	1	1966	2113	5	31	1872	1846	8	18	1060	1075	6	-2	1956	2008
6	66	672	663	-5	3	593	626	5	33	1778	1776	8	20	538	576	6	0	1802	1830
6	68	607	502	-5	5	3606	3512	5	35	372	370	8	22	591	591	6	2	881	922
6	70	737	730	-5	7	4430	4263	5	37	893	911	8	24	1820	1871	6	4	1840	843
6	72	1978	1967	-5	9	1107	1094	5	39	1284	1305	8	26	2320	2310	6	6	1857	1879
6	74	2209	2144	-5	11	1532	1557	5	41	1059	1010	8	28	636	635	6	8	1234	1267
6	76	473	523	-5	13	2049	2030	5	43	1124	1046	8	30	1829	1916	8	-18	1128	1200
6	78	1711	1646	-5	15	1591	1560	5	45	1643	1650	8	32	3178	3295	8	-16	1547	1557
6	80	2366	2297	-5	17	428	447	5	47	2244	2255	8	34	2393	2527	8	-14	781	830
6	82	1600	1560	-5	19	704	738	5	49	2677	2668	8	36	2547	2540	8	-12	473	498
6	84	1590	1607	-3	-11	1834	1746	5	51	1497	1541	8	38	3660	3594	8	-10	2320	2312
6	86	2069	2102	-3	-9	3128	2996	5	53	1267	1279	8	40	1520	1474	8	-8	2670	2625
6	88	845	878	-3	-7	1572	1612	5	55	1737	1708	8	42	1357	1305	8	-6	811	852
6	90	1007	1063	-3	-5	1071	1117	5	57	1702	1659	8	44	1383	1373	8	-4	1176	1230
6	92	1828	1765	-3	-3	2893	2993	5	59	1702	1659	8	46	1676	1742	8	-2	2345	2457
6	94	1069	1058	-3	-1	3364	3508	5	61	1702	1659	8	48	1760	1742	8	0	1934	1940
6	96	1484	1411	-3	1	1295	1342	5	63	1702	1659								

Table 4 (continued)

I	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL
H = 8*				***H = 8****				***H = 8****				***H = 8****				***H = 8****			
14	-16	704	721	1	-13	2104	2077	-8	-8	332	328	10	-8	943	903	7	-3	1425	1425
14	-12	699	675	1	-11	720	670	-8	-6	687	697	10	-6	1308	1352	7	-1	430	428
14	-10	1189	1123	1	-7	2832	2666	-8	-4	1514	1524	10	-4	894	861	7	1	694	675
14	-8	818	817	1	-5	2452	2366	-8	-2	1637	1657	10	0	868	882	7	3	1091	1098
14	-4	901	950	1	-3	407	429	-8	2	1292	1307	10	2	897	943	9	-13	986	1031
14	-2	1097	1112	1	-1	2267	2246	-8	4	1813	1815	12	-12	874	903	9	-11	1275	1259
16	-10	1108	1150	1	1	3461	3453	-8	6	967	1011	12	-8	847	820	9	-9	399	481
16	-8	593	676	1	3	1793	1814	-8	10	1216	1210	12	-6	1275	1286	9	-5	940	967
H = 8*				***H = 8****				***H = 8****				***H = 8****				***H = 8****			
-15	1	553	562	1	7	1939	1868	-8	14	761	747	12	-4	799	840	9	-3	1140	1170
-15	3	1118	1078	1	9	2118	2129	-6	10	804	848	-13	3	298	282	9	-1	400	486
-15	5	846	837	1	11	839	809	-6	-6	691	739	-13	5	600	612	11	-9	532	548
-15	7	355	129	1	13	323	338	-6	-8	1490	1534	-13	7	1223	1186	11	-7	350	326
-15	9	852	803	3	-17	628	630	-6	-2	1366	1348	-13	9	793	785	11	-5	1072	1084
-15	11	1218	1298	3	-15	1610	1590	-6	2	1242	1226	-11	-3	646	657	***H = 8****			
-15	13	695	767	3	-13	1360	1357	-6	4	1748	1704	-11	-1	1053	1150	-10	0	695	754
-13	-3	777	793	3	-9	1220	1206	-6	6	987	951	-11	1	891	797	-10	2	790	743
-13	-1	418	147	3	-7	2294	2242	-6	10	1125	1092	-11	5	1075	1107	-10	6	675	579
-13	1	588	647	3	-5	1575	1601	-6	12	1453	1430	-11	7	1513	1409	-10	8	816	888
-13	3	1092	1104	3	-3	447	430	-6	14	720	680	-11	9	668	724	-8	2	366	395
-13	5	860	790	3	-1	2080	2158	-4	-12	1015	1016	-11	11	231	224	-8	0	969	888
-13	9	910	842	3	1	2281	2260	-4	-10	1082	1099	-9	-3	978	901	-8	2	921	903
-13	11	1230	1294	3	3	1080	1060	-4	-8	445	516	-9	-1	1270	1287	-8	6	703	738
-13	13	724	739	3	7	1480	1492	-4	-6	725	720	-9	1	638	685	-8	8	1089	1086
-11	-5	932	943	3	9	1516	1527	-4	-4	2123	2134	-9	3	810	378	-8	10	715	686
-11	-3	1110	1128	3	11	458	450	-4	-2	1903	1876	-9	5	1280	1195	-6	-6	1009	1032
-11	-1	383	376	5	-17	450	487	-4	2	1524	1545	-9	7	1289	1374	-6	-4	527	315
-11	1	1029	990	5	-15	1409	1332	-4	4	2470	2533	-9	9	548	561	-6	-2	605	636
-11	3	1666	1655	5	-13	1464	1473	-4	6	1523	1472	-9	11	374	395	-6	0	1313	1346
-11	5	1025	997	5	-11	520	551	-4	10	1211	1175	-9	13	763	797	-6	2	1102	1083
-11	7	796	853	5	-9	1434	1344	-4	12	1826	1725	-7	-7	636	618	-6	6	1071	1073
-11	9	1783	1797	5	-7	2471	2490	-4	14	841	842	-7	-3	1087	1083	-6	8	1381	1408
-11	11	1033	1065	5	-5	1447	1440	-2	-14	545	610	-7	-1	1423	1475	-6	10	810	786
-9	-9	291	298	5	-3	377	295	-2	-12	1561	1563	-7	1	730	679	-6	-8	1227	1246
-9	-7	469	624	5	-1	1345	1378	-2	-10	1391	1354	-7	5	1091	1045	-4	-6	1099	1017
-9	-5	1643	1632	5	1	2619	2544	-2	-6	1625	1613	-7	7	1361	1353	-4	-2	1301	1315
-9	-3	1482	1453	5	3	1528	1486	-2	-4	2787	2626	-7	9	574	617	-4	0	1593	1586
-9	1	1400	1412	5	7	1290	1265	-2	-2	1895	1744	-7	11	424	386	-4	2	730	712
-9	3	2393	2476	5	9	1357	1365	-2	2	2676	2541	-7	13	827	841	-4	4	328	369
-9	5	1669	1646	7	-17	771	795	-2	4	2926	2919	-5	-9	1292	1320	-4	6	1359	1331
-9	7	1962	1516	7	-15	1708	1747	-2	6	1075	1070	-5	-7	831	830	-4	8	1463	1425
-9	9	1996	1969	7	-13	1293	1307	-2	8	507	499	-5	-5	1248	1329	-4	10	478	466
-9	11	942	948	7	-9	1784	1789	-2	10	1572	1516	-5	-1	2075	2052	-2	-8	1285	1257
-9	13	403	353	7	-7	2837	2834	-2	12	1569	1545	-5	1	1207	1207	-2	-6	625	590
-7	-11	725	786	7	-5	1719	1736	-2	14	401	426	-5	3	435	446	-2	-2	1138	1097
-7	-9	961	995	7	-3	389	403	0	-14	1080	1130	-5	5	1477	1486	-2	0	1426	1406
-7	-7	1219	1239	7	-1	2232	2244	0	-12	1803	1747	-5	7	1526	1495	-2	2	627	646
-7	-5	2254	2252	7	1	2213	2178	0	-10	853	811	-5	9	599	621	-2	4	445	471
-7	-3	1377	1421	7	3	916	872	0	-8	405	338	-5	11	609	583	-2	6	1092	1093
-7	-1	718	668	7	5	431	418	0	-6	1926	1781	-5	13	1132	1176	0	-10	813	811
-7	1	2404	2514	7	7	1461	1473	0	-4	3099	2903	-3	-11	1118	1159	0	-8	1375	1312
-7	3	2813	2960	9	-17	1031	1069	0	-2	1235	1158	-3	-9	1560	1534	0	-6	803	786
-7	5	1155	1084	9	-15	1647	1598	0	0	1153	1171	-3	-7	639	627	0	-2	1417	1326
-7	7	783	786	9	-13	830	841	0	2	2353	2294	-3	-5	740	748	0	0	1658	1638
-7	9	1768	1744	9	-11	374	466	0	4	2145	2090	-3	-3	1448	2080	0	2	690	678
-7	11	1874	1844	9	-9	2069	2084	0	6	711	715	-3	-1	2248	2218	0	4	936	939
-7	13	488	515	9	-7	2412	2446	0	8	669	684	-3	1	469	499	0	6	1055	1080
-7	15	934	913	9	-5	789	738	0	10	1360	1364	-3	3	1251	1206	2	-10	1085	1102
-7	17	1126	1140	9	-3	901	895	0	12	968	975	-3	5	1733	1700	2	-8	1599	1553
-5	-13	1025	1125	9	-1	1707	1652	2	-14	1131	1116	-3	7	1261	1252	2	-6	751	737
-5	-11	638	653	9	1	1456	1444	2	-12	1656	1618	-3	11	1110	1076	2	-4	457	501
-5	-9	446	423	9	3	456	414	2	-10	672	683	-3	13	409	478	2	-2	1570	1560
-5	-7	1330	1381	9	5	740	757	2	-8	543	555	-1	-11	1338	1210	2	0	1626	1664
-5	-5	1903	1945	11	-17	1072	1053	2	-6	1817	1773	-1	-9	1295	1304	2	2	603	634
-5	-3	893	913	11	-15	1130	1123	2	-4	2115	2081	-1	-5	1069	1012	2	4	604	604
-5	-1	737	770	11	-13	370	332	2	-2	788	752	-1	-3	2046	1904	2	6	1194	1214
-5	1	215	219	11	-11	628	582	2	0	655	626	-1	-1	1527	1472	4	-12	441	445
-5	3	2371	2395	11	-9	1520	1551	2	2	1949	1881	-1	3	1175	1153	4	-10	1324	1352
-5	5	777	771	11	-7	1577	1558	2	4	1856	1830	-1	5	1522	1502	4	-8	1453	1421
-5	7	756	778	11	-5	409	382	2	6	429	418	-1	7	820	786	4	-6	820	864
-5	9	1579	1481	11	-3	724	719	2	8	654	627	-1	9	256	161	4	-2	1556	1631
-5	11	1261	1224	11	-1	1151	1184	2	10	931	958	-1	11	447	446	4	0	1333	1322
-3	13	1460	1409	13	-13	883	931	4	-14	1202	1207	1	-13	440	431	4	4	889	879
-3	-11	697	762	13	-11	981	986	4	-12	1972	1888	1	-11	1285	1255	6	-10	1038	1122
-3	-9	1407	1345	13	-9	482	502	4	-10	898	934	1	-9	1213	1213	6	-8	821	879
-3	-7	2699	2661	13	-7	338	281	4	-6	1543	1555	1	-5	853	847	6	-6	729	735
-3	-5	1899	1512	13	-5	1148	1145	4	-4	2431	2377	1	-3	1808	1666	6	-2	1114	117

TABLE 5: ATOMIC POSITIONAL PARAMETERS^a

ATOM	x	y	z
Re	0.11870 (5)	-0.01029 (3)	-0.06551 (2)
Si	-0.0875 (3)	-0.1386 (2)	-0.0709 (2)
C1	0.271 (1)	-0.0259 (7)	-0.1477 (7)
C2	-0.041 (1)	0.0202 (7)	-0.1282 (7)
C3	0.278 (1)	-0.0428 (8)	-0.0045 (7)
C4	-0.409 (2)	-0.240 (1)	-0.1392 (8)
C5	-0.261 (1)	-0.1901 (8)	-0.1570 (6)
C6	-0.006 (1)	-0.2389 (8)	-0.0638 (6)
C7	0.075 (2)	-0.3048 (9)	-0.1401 (8)
O1	0.364 (1)	-0.0351 (7)	-0.1945 (6)
O2	-0.129 (1)	0.0377 (7)	-0.1691 (6)
O3	0.377 (1)	-0.0623 (8)	0.0298 (6)

^aStandard deviations in parentheses refer to last digit quoted.

TABLE 6: THERMAL PARAMETERS (\AA^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B^a (\text{\AA}^2)$
Re	0.0380(3)	0.0406(3)	0.0331(3)	0.0010(2)	0.0037(2)	0.0175(2)	2.98
Si	0.0471(14)	0.0394(13)	0.0379(13)	-0.0013(10)	0.0018(10)	0.0176(11)	3.37
C1	0.062(7)	0.048(6)	0.048(6)	-0.006(5)	-0.001(5)	0.021(5)	4.36
C2	0.064(7)	0.043(6)	0.054(6)	0.000(5)	0.013(5)	0.020(5)	4.39
C3	0.052(6)	0.058(6)	0.054(6)	0.004(5)	0.016(5)	0.026(5)	4.35
C4	0.060(8)	0.098(11)	0.068(8)	-0.028(7)	-0.004(6)	0.037(7)	6.38
C5	0.055(6)	0.060(6)	0.045(6)	-0.008(5)	-0.005(5)	0.020(5)	4.53
C6	0.076(8)	0.052(6)	0.046(6)	0.008(5)	0.013(5)	0.027(5)	4.49
C7	0.116(11)	0.068(8)	0.068(8)	0.043(8)	0.028(7)	0.030(7)	6.50
O1	0.086(7)	0.103(8)	0.076(6)	0.004(5)	0.034(5)	0.036(6)	7.19
O2	0.082(6)	0.097(7)	0.063(5)	0.026(5)	-0.003(4)	0.049(5)	5.99
O3	0.054(5)	0.129(8)	0.095(7)	0.024(5)	0.006(4)	0.076(6)	6.53

^aEquivalent isotropic thermal parameter.

TABLE 7: INTRAMOLECULAR DISTANCES AND ANGLES

INTRAMOLECULAR DISTANCES^a (Å)

Re-Re' ^b	3.084 (1)	Si-C6	1.88 (1)
Re-Si	2.533 (2)	Cl-O1	1.14 (2)
Re-Si'	2.535 (3)	C2-O2	1.17 (1)
Re-Cl	1.94 (1)	C3-O3	1.17 (1)
Re-C2	1.96 (1)	C4-C5	1.54 (1)
Re-C3	1.97 (1)	C6-C7	1.52 (2)
Si-C4	1.885 (8)		

INTRAMOLECULAR ANGLES^a (DEGREES)

Re-Re'-Cl ^b	178.5 (3)	C3-Re-C2	179.1 (5)
Re-Re'-C2	91.0 (3)	C4-Si-C6	108.5 (5)
Re-Re'-C3	89.3 (3)	Re-Si-Re'	74.9 (1)
Re-Re'-Si	52.6 (1)	Re-Cl-O1	178.0 (9)
Re-Re'-Si'	52.5 (1)	Re-C2-O2	175.7 (9)
Cl-Re-C3	89.4 (4)	Re-C3-O3	177.5 (9)
Cl-Re-C2	90.3 (4)	Si-C4-C5	114.5 (8)
Cl-Re-Si	126.6 (3)	Si-C6-C7	115.0 (10)
Cl-Re-Si'	128.3 (3)		

^aStandard deviations in parentheses refer to last digit quoted.

^bPrimed atoms related by an inversion centre.

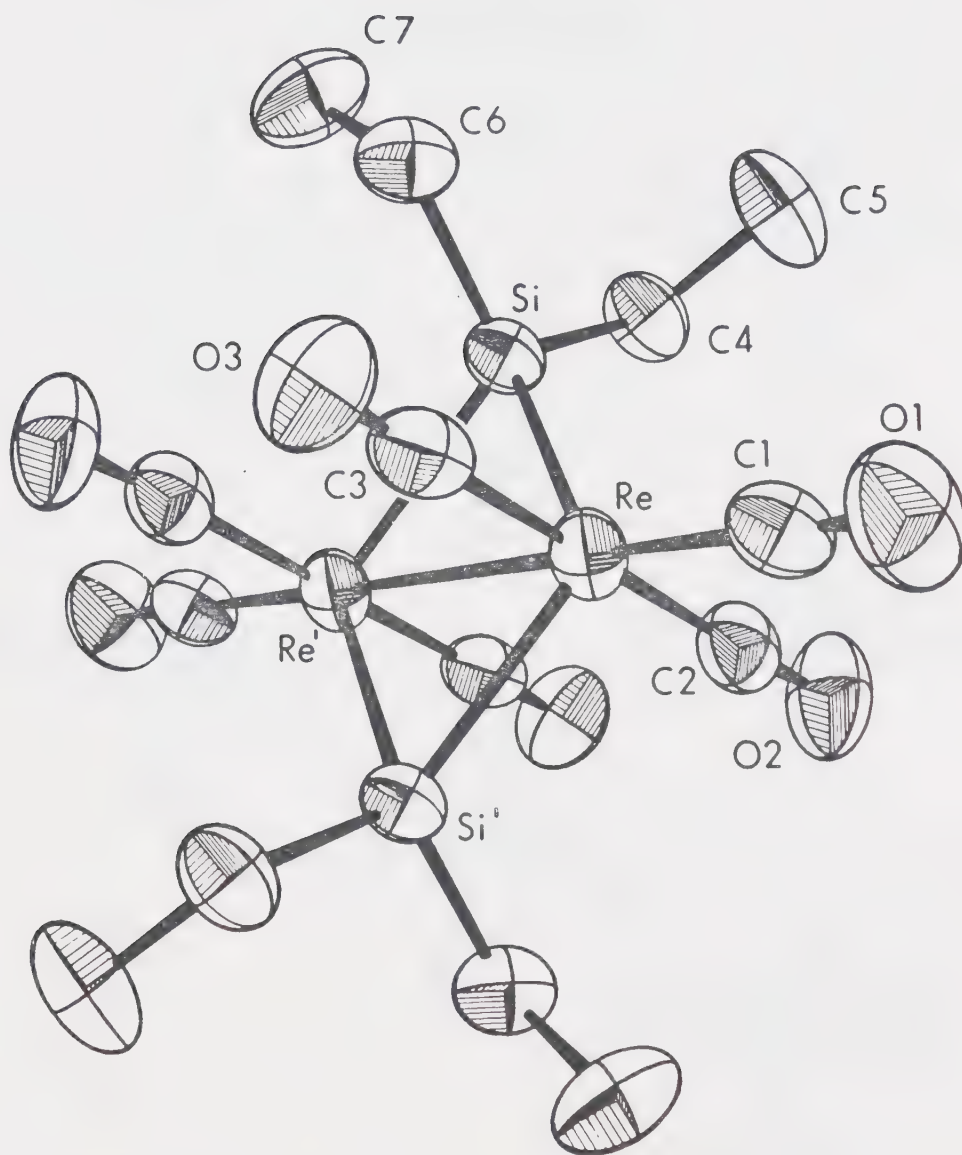


Fig. 3: A PERSPECTIVE VIEW OF $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$.

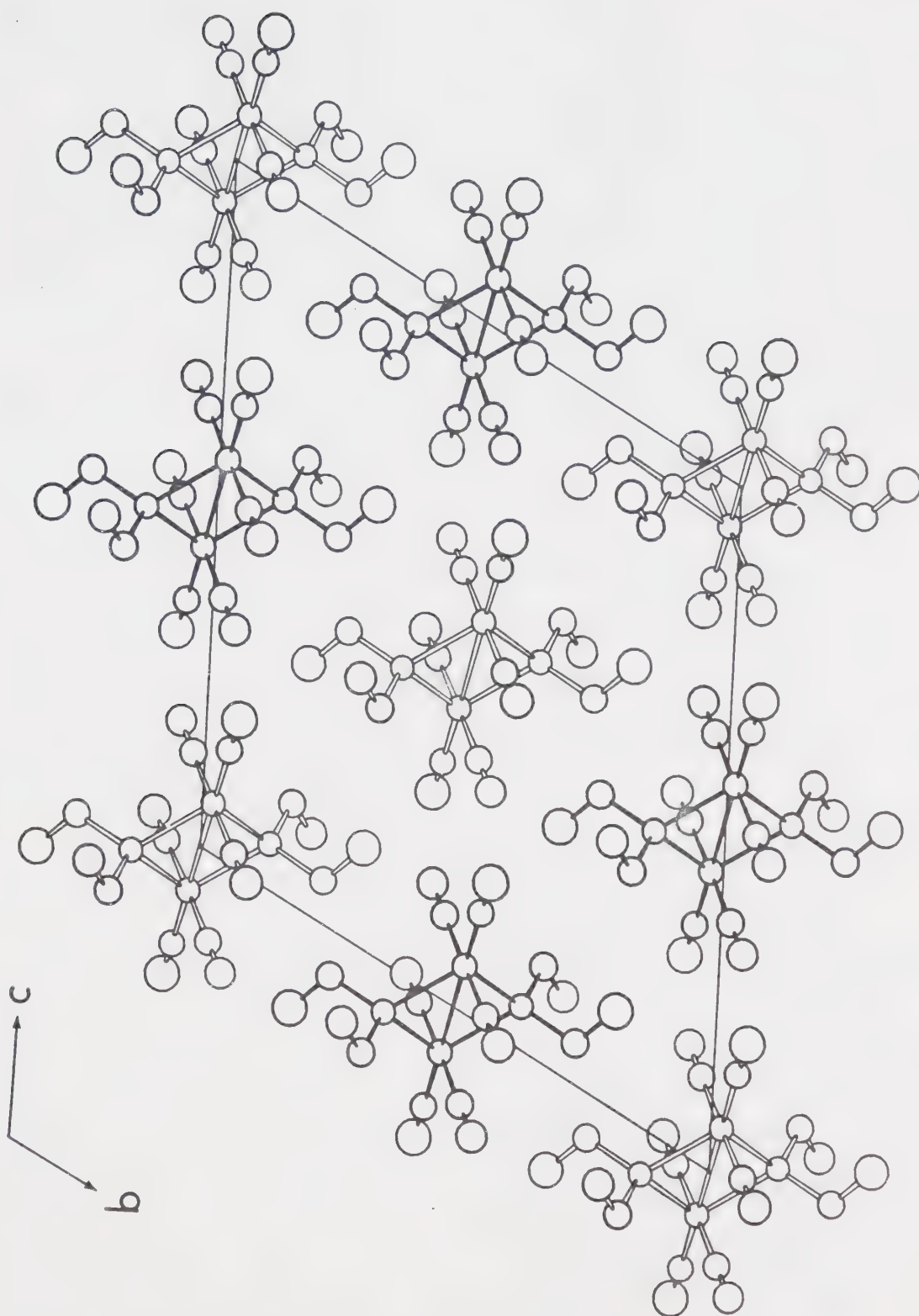


Fig. 4: PACKING DIAGRAM FOR $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$,
PROJECTED ON bc PLANE.

DESCRIPTION OF STRUCTURE

$\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ has approximate C_{2h} molecular symmetry. Its molecular structure is shown in Figure 3. The molecule is composed of a central cluster of two rhenium and two silicon atoms in the shape of a rhombus, with like atoms at opposing corners, and a bond joining the two rheniums across the shorter diagonal. One carbonyl group on each rhenium lies approximately along the Re-Re axis, while the other four lie above and below the plane of the rhombus, two on each rhenium. The ethyl groups are bonded two to each silicon, one above and one below the rhombus plane, giving the silicon atoms a distorted tetrahedral environment.

The Re-Re distance is $3.084(1) \text{ \AA}$, compared with $3.121(2) \text{ \AA}$ in $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$,^{62,65} $3.001(1) \text{ \AA}$ in $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$,⁶⁴ and 3.02 \AA in $\text{Re}_2(\text{CO})_{10}$,^{45,82,83} and thus is again consistent with a Re-Re single bond. This is further substantiated by the acute Re-Si-Re angle $[74.9(1)^\circ]$. The average Re-C (carbonyl) distance is 1.96 \AA and the average C-O distance is 1.16 \AA . These agree well with the carbonyl distances in other rhenium carbonyl derivatives.^{62,64,65} The Re-C and C-O bonds along the Re-Re bond are not significantly different from the two *trans* carbonyl

groups perpendicular to the Re_2Si_2 plane. In addition the average Si-C (ethyl) distance (1.88 \AA) and C-C distance (1.53 \AA) both agree with the sums of the Si-C (sp^3) and C(sp^3)-C(sp^3) covalent radii^{27,84} (1.91 \AA and 1.54 \AA respectively).

The Re-Si bond lengths (2.534 \AA) are in close agreement with those found in $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$ ^{62,65} and $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$,⁶⁴ (2.544 \AA and 2.542 \AA respectively). This was not expected if bridging hydrogens were present in the two hydrides. Rather a difference in bridged and unbridged Re-Si bonds, analogous to that observed in $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ ⁶⁶ was expected. A complete discussion of this phenomenon follows in Chapter IV, with emphasis on the existence of bridging hydrogens and their relation to the transition metal-silicon bonds.

CHAPTER III: THE CRYSTAL AND MOLECULAR
STRUCTURE OF DIHYDRIDO TRICARBONYL RHENIUM
BIS (μ -DIETHYLSILICON) TETRACARBONYL RHENIUM,



EXPERIMENTAL

The sample of $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$, supplied by Dr. Graham and Mr. Hoyano,⁶³ was sublimed in a sealed tube to give crystals that were suitable for a single crystal diffraction study. The crystals produced were clear colourless plates. Preliminary photographs showed $\bar{1}$ Laué symmetry and no systematic absences, consistent with the triclinic space groups $P1$ and $P\bar{1}$. Precise lattice parameters were obtained at 22°C from the 2θ angles of 17 reflections centred on a Picker manual four circle diffractometer using CuK_{α_1} X-radiation ($\lambda = 1.54051 \text{ \AA}$). The parameters are: $a = 8.664(1) \text{ \AA}$, $b = 14.066(2) \text{ \AA}$, $c = 9.343(1) \text{ \AA}$, $\alpha = 96.57(2)^\circ$, $\beta = 93.86(1)^\circ$, $\gamma = 91.63(1)^\circ$. A Delaunay reduction⁶⁹ showed no higher symmetry. The experimental density [$2.21(2) \text{ g cm}^{-3}$] determined by floatation in aqueous Clerici's solution, is in acceptable agreement with that calculated (2.23 g cm^{-3}) assuming two molecules of molecular weight 742.9

a.m.u. in a unit cell of volume 1107 \AA^3 .

Intensity data were collected on the Picker manual diffractometer using CuK_{α} X-radiation monochromated using the (002) reflecting plane of an oriented graphite crystal and using a 2° take-off angle. The crystal was aligned with its a^* axis coincident with the ϕ axis of the diffractometer. The crystal faces were identified and the perpendicular distances between parallel faces of the same form measured as: $\{1,0,0\}$, $7.7 \times 10^{-2} \text{ mm}$; $\{0,1,0\}$, $5.3 \times 10^{-2} \text{ mm}$; $\{0,0,1\}$, $1.9 \times 10^{-2} \text{ mm}$. A coupled $\omega/2\theta$ scan technique was used with a 2θ scan speed of $2^\circ/\text{min}$ to collect all reflections with $2\theta \leq 125^\circ$. Initially a peak scan of 90 secs. (3 deg.) and a stationary background count of 20 secs. at the limits of the scan were used, however as the crystal decomposed and the mosaic spread increased this was changed to 99 sec. peak scans and 19 sec. backgrounds.⁸⁵ A scintillation counter in conjunction with a pulse height analyser, tuned to accept 95% of the CuK_{α} peak, was used to detect the scattered X-rays. Nine well distributed standard reflections were monitored at approximately 10 hr. intervals to assess decomposition effects. The 2836 unique reflections collected were reduced to

2020 significant observations using the criterion that a peak was significantly above background for $I/\sigma(I) \geq 3.0$, where $\sigma(I)$ was computed as described in Chapter II. The data were then reduced to structure factor amplitudes by correction for Lorentz, polarization, decomposition, and absorption effects. The decomposition was approximately linear with time and no significant $\sin \theta/\lambda$ dependence was observed. Total decomposition for the data collection was about 13%. Standard deviations, $\sigma(F)$, in the structure factors were computed as described in the previous chapter using a "p factor" of 0.03.

The high linear absorption coefficient⁸⁶ of 216.78 cm^{-1} for CuK_{α} X-radiation, and the platy habit of the crystals gave rise to a considerable range of transmission factors (0.14 - 0.47). The absorption correction was verified experimentally by investigation of the behavior of I_{h00} as a function of ϕ . The internal consistency of the corrected intensities showed maximum deviations of less than 10% from the mean and was considered acceptable.

TABLE 8: PATTERSON VECTORS^a FOR $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$

u	v	w	Multiplicity	Relative Peak Height ^c	Assignment ^b
0.167	0.200	0.080	2	523	$(x_1-x_2), (y_1-y_2), (z_1-z_2)$
0.210	0.500	0.500	2	520	$(x_2+x_1), (y_2+y_1), (z_2+z_1)$
-0.384	0.300	0.403	1	288	$2x_1, 2y_1, 2z_1$
0.036	0.325	0.414	1	231	$2x_2, 2y_2, 2z_2$
0.090	-0.150	0.070	2	184	$-(x_1-x_4), -(y_1-y_4), -(z_1-z_4)$
0.254	0.050	0.145	2	169	$(x_1-x_3), (y_1-y_3), (z_1-z_3)$

^aCentrosymmetrically related vectors are not listed.

^b $(x_1, y_1, z_1), (x_2, y_2, z_2), (x_3, y_3, z_3)$, and (x_4, y_4, z_4) are the coordinates of the Re1, Re2, Si1 and Si2 atoms respectively.

^cExpected Peak Heights calculated as in Chapter II.

Re₁-Re₂, 444; 2Re, 222; Re-Si, 166.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson^{73,74} map was computed between the limits $-0.5 \leq u \leq 0.5$, $-0.5 \leq v \leq 0.5$, and $0.0 \leq w \leq 0.5$. The rhenium-rhenium vectors were readily identified in the Patterson map and a consistent solution for the coordinates of the two independent rhenium atoms was found to be: Re1, (0.185, 0.363, 0.287) and Re2, (0.018, 0.163, 0.207). Image seeking around the origin and Re-Re vectors provided consistent solutions for the silicon atom coordinates as: Si1, (-0.069, 0.313, 0.142), and Si2, (0.275, 0.213, 0.357). The major vectors and their assignments are shown in Table 8.

A resumé of the refinement is shown in Table 9.

TABLE 9: REFINEMENT OUTLINE

MODEL	R_1	R_2
1) Rhenium and Silicon atoms isotropic	0.166	0.238
2) All non-hydrogen atoms isotropic	0.106	0.131
3) Decomposition and Absorption Corrections	0.061	0.078
4) Re and Si anisotropic temperature factors	0.047	0.064
5) All non-hydrogen atoms with anisotropic temperature factors	0.040	0.057

Structure factors were calculated using the atomic scattering factors⁷⁵ for the neutral atoms for rhenium, silicon, carbon, and oxygen. The real and imaginary parts of anomalous dispersion corrections⁷⁶ were applied to the rhenium and silicon scattering factors.⁷⁷ All non-hydrogen atoms were located from an electron density difference map phased on model 1 . Refinement of the model with all temperature factors anisotropic was suggested by features on an electron density difference map phased on model 4 , and was verified by a Hamilton's R Test⁷⁹ at the 0.005 significance level. Anisotropic temperature factors were of the form:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] .$$

In an attempt to locate the hydrogen atoms an electron density difference map was calculated, phased on model 5 . The highest features were of the approximate magnitude $1.1e^{-3} \text{ \AA}^{-3}$ and were located in the vicinity of the rhenium atoms, but could not be interpreted as hydrogen atom peaks. Similarly no peaks were observed in the positions predicted for the methylene hydrogens of the ethyl groups. The inability to locate hydrogens in this structure is due to similar problems as encountered for $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$.

The scattering is dominated too much by the heavy rhenium atoms and hampers location of the hydrogens. Also, it is probable that residual absorption effects severely limit the data. This is especially true in this structure due to the wide range of transmission factors.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 10. Table 11 contains the final fractional coordinates of all atoms except hydrogen, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic thermal parameters⁸⁰ (U's) and equivalent isotropic B's⁸¹ of all atoms are shown in Table 12 and bond lengths and angles are given in Tables 13 and 14 respectively. The bond lengths and angles along with their standard deviations were obtained from ORFFE. Fig. 5 shows a three dimensional representation of the molecule. Least squares plane calculations are shown for the Re_2Si_2 plane (Table 15) showing the deviations of the Re and Si atoms from the plane and also the distances of the carbonyl groups, C202, C303 and C606, from

this plane. Also the plane through the four carbonyl groups perpendicular to the Re_2Si_2 plane is calculated and also selected atom distances from this plane.

TABLE 10: OBSERVED AND CALCULATED STRUCTURE
FACTOR AMPLITUDES (ELECTRONS X 10)

R	L	POBS	FCAL	R	L	POBS	FCAL	R	L	POBS	FCAL	R	L	POBS	FCAL	R	L	POBS	FCAL
-13	5	357	378	7	-2	488	508	-7	0	427	427	0	6	365	362	7	-1	279	256
-12	4	575	599	7	-1	1455	1423	-7	1	1659	1731	0	7	411	404	7	1	334	319
-12	5	357	377	7	0	497	498	-7	2	421	440	0	8	524	518	7	2	833	835
-12	6	339	350	7	1	427	404	-7	3	947	978	0	9	344	350	7	3	556	610
-11	4	372	373	7	3	525	543	-7	4	288	263	1	-9	189	185	7	4	1097	1149
-11	5	311	290	7	4	350	344	-7	5	873	843	1	-8	334	332	7	5	461	468
-10	4	426	415	7	5	845	865	-7	6	179	175	1	-7	658	665	7	6	705	716
-10	6	177	184	7	6	394	406	-7	7	428	418	1	-6	668	670	7	7	253	257
-10	7	263	256	7	7	500	546	-6	-8	192	203	1	-5	514	521	7	8	293	325
-10	8	384	418	8	-2	436	463	-6	-4	568	551	1	-4	1275	1278	8	-8	312	302
-9	5	339	367	8	2	636	632	-6	-3	300	283	1	-3	2069	2025	8	-7	563	575
-9	6	205	310	8	3	551	567	-6	-2	1410	1468	1	-2	1176	1174	8	-6	330	320
-9	7	571	590	8	4	942	1016	-6	-1	755	748	1	-1	1616	1557	8	-5	425	400
-9	8	287	324	8	5	473	547	-6	0	2049	2042	1	0	889	820	8	-4	259	283
-8	4	583	607	8	6	694	787	-6	1	663	668	1	1	209	228	8	-3	253	244
-8	5	314	316	8	7	268	269	-6	2	1359	1479	1	2	392	385	8	-1	239	224
-8	6	813	821	9	-2	334	344	-6	3	233	231	1	3	486	494	8	0	368	340
-8	7	247	261	9	-1	839	798	-6	4	265	272	1	4	1044	1055	8	1	1016	962
-8	8	644	658	9	0	354	349	-6	5	180	155	1	5	1065	1060	8	2	618	627
-7	3	1244	1334	9	1	790	783	-5	-7	323	317	1	6	740	722	8	3	1249	1281
-7	4	466	455	9	2	596	596	-5	-6	190	170	1	7	668	660	8	4	419	434
-7	5	909	907	9	3	1094	1072	-5	-5	842	812	1	8	600	595	8	5	786	850
-7	6	225	217	9	4	537	550	-5	-4	291	277	1	9	351	334	8	6	211	234
-7	7	608	594	9	5	721	741	-5	-3	1567	1528	2	-9	393	399	8	7	230	241
-7	8	196	168	9	6	330	335	-5	-2	781	751	2	-8	617	601	9	-8	348	350
-7	9	202	240	9	7	228	237	-5	-1	1540	1577	2	-7	740	741	9	-7	206	104
-6	2	1844	1927	10	-3	325	333	-5	0	904	875	2	-6	998	971	9	-6	434	466
-6	3	479	500	10	-2	996	963	-5	1	1585	1629	2	-5	781	831	9	-3	231	234
-6	4	1021	1011	10	-1	705	660	-5	2	167	176	2	-4	751	767	9	-2	617	595
-6	5	198	206	10	0	1061	994	-5	3	150	146	2	-3	1242	1203	9	-1	370	367
-6	6	385	378	10	1	490	493	-5	4	647	648	2	-2	371	391	9	0	1277	1226
-5	2	500	503	10	2	810	785	-5	5	324	315	2	-1	297	231	9	1	401	363
-5	3	1160	1130	10	3	499	482	-5	6	737	712	2	0	202	44	9	2	1101	1058
-5	4	182	205	10	4	553	540	-5	7	337	308	2	1	702	675	9	3	327	305
-5	5	748	454	10	5	239	229	-5	8	458	458	2	2	631	648	9	4	711	723
-5	6	417	417	10	6	226	236	-4	-8	437	445	2	3	1234	1233	9	5	270	230
-5	7	444	478	11	-3	827	794	-4	-7	000	378	2	4	1465	1457	9	6	152	138
-5	8	213	206	11	-2	665	615	-4	-6	1138	1118	2	5	1366	1398	10	-5	645	660
-4	5	188	184	11	-1	1001	920	-4	-5	482	474	2	6	888	876	10	-4	408	390
-4	6	888	895	11	0	547	508	-4	-4	1069	1013	2	7	694	702	10	-3	883	877
-4	7	231	210	11	1	463	455	-4	-3	684	671	2	8	444	437	10	-2	475	451
-4	8	940	891	11	2	197	213	-4	-2	1138	1079	2	9	148	153	10	-1	1226	1160
-3	1	748	644	11	3	255	241	-4	-1	227	244	3	-9	504	493	10	0	337	310
-3	2	492	504	12	-3	604	531	-4	0	1249	1153	3	-8	615	592	10	1	712	686
-3	3	352	360	12	-2	690	654	-4	1	131	109	3	-7	744	733	10	2	247	219
-3	4	1450	1440	12	-1	564	519	-4	2	192	234	3	-6	709	717	10	3	468	460
-3	5	196	186	12	0	268	254	-4	3	147	172	3	-5	300	304	11	-6	511	510
-3	6	1367	1351	12	1	181	162	-4	4	1136	1136	3	-3	227	210	11	-5	210	258
-3	7	177	116	12	2	259	254	-4	5	715	736	3	-2	558	528	11	-4	998	975
-3	8	552	560	13	-4	372	326	-4	6	1241	1238	3	-1	808	549	11	-3	276	295
-2	1	142	135	13	-3	432	427	-4	7	544	512	3	0	703	694	11	-2	909	842
-2	2	1071	1056	13	-2	341	313	-4	8	724	730	3	1	1324	1273	11	-1	173	182
-2	3	425	428	13	-1	174	167	-4	9	214	244	3	2	952	912	11	0	487	471
-2	4	1402	1480	13	1	145	151	-3	-8	399	371	3	3	1323	1262	11	1	238	252
-2	5	1265	1297	13	2	305	280	-3	-7	1050	1030	3	4	1436	1434	12	-6	169	146
-2	6	630	631	13	3	442	431	-3	-6	636	635	3	5	1002	981	12	-5	782	704
-1	1	2901	3068	14	-4	152	120	-3	-5	1068	1070	3	6	757	741	12	-4	177	164
-1	2	147	100	14	0	199	195	-3	-4	497	481	3	7	320	324	12	-3	638	623
-1	3	1664	1636	14	1	267	284	-3	-3	714	730	4	-9	406	396	12	-2	227	236
-1	4	311	301	14	2	401	400	-3	-2	233	201	4	-8	452	419	12	1	297	270
-1	5	897	919	14	3	191	105	-3	-1	191	105	4	-7	369	375	12	0	459	464
-1	6	459	458	14	-2	221	273	-3	0	1443	1386	4	-5	208	190	13	-5	154	88
0	2	1945	1850	14	2	202	220	-3	2	458	455	4	-4	471	484	13	-4	362	344
0	3	290	287	14	3	337	332	-3	3	1062	1133	4	-3	1118	1105	13	0	416	408
0	4	708	725	13	-4	205	214	-3	4	985	958	4	-2	153	153	13	1	162	153
0	5	322	333	13	-1	275	262	-3	5	1744	1715	4	-1	1304	1313	13	2	632	623
1	1	2223	2085	13	1	560	574	-3	6	811	814	4	0	1450	1386	14	-1	546	521
1	2	173	186	13	2	703	708	-3	7	841	821	4	1	1660	1624	14	1	635	630
1	3	745	688	13	3	487	485	-3	8	324	343	4	2	750	728	14	2	781	801
1	4	241	226	12	-2	336	332	-3	9	248	283	4	3	1091	1013	14	3	184	180
1	5	574	551	12	0	791	800	-2	-9	308	299	4	4	646	606	14	4	365	374
1	6	163	135	12	1	1056	1047	-2	-8	641	620	4	5	594	555	14	5	241	242
1	7	842	801	12	2	472	473	-2	-7	470	451	4	6	274	248	14	6	151	160
1	8	480	460	12	3	242	233	-2	-6	977	968	4	7	173	142	14	7	657	662
2	2	1262	1192	11	-5	238	184	-2	-5	292	332	4	8	167	147	13	0	340	335
2	3	208	277	11	-3	494	495	-2	-4	213	200	4	9	265	302	13	1	552	527
2	4	159	158	11	-1	853	867	-2	-2	159	162	5	-9	160	182	13	2	392	382
2	5	1266	1237	11	1	1134	1118	-2	-1	804	759	5	-6	269	252	13	3	546	518
2	6	278	285	11	2	633	637	-2	0	1468	1556	5	-5	432	435	13	4	275	283
2	7	1474	1445	11	3	236	279	-2	1	817	968	5	-4	1465	1439	13	5	321	314
2	8	245	255	10	-6	409	460	-2	2	1854	1808	5	-3	1245	1218	13	6	261	248
2	9	719	710	10	-4	763	779	-											

Table 10 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
-2	-5	317	335	7	4	1085	1169	-6	-4	188	162	2	-3	611	630	10	2	180	168
-2	-2	1206	1168	7	5	212	201	-6	-3	1438	1464	2	-2	452	450	10	3	210	238
-2	-2	812	783	7	6	882	503	-6	-1	1090	1085	2	-1	1297	1327	10	4	458	460
-2	-1	1628	1521	8	-3	361	356	-6	3	455	465	2	0	740	778	10	5	345	340
-2	0	595	610	8	-1	1054	1046	-6	5	586	587	2	2	1358	1355	-8	0	685	676
-2	1	2557	2564	8	0	421	418	-6	6	155	93	2	3	1186	1203	-8	1	712	719
-2	2	546	553	8	1	1880	1806	-6	7	848	833	2	4	575	558	-8	2	501	521
-2	3	1411	1451	8	2	349	325	-5	-8	523	542	2	5	344	360	-8	3	498	534
-2	4	303	298	8	3	958	985	-5	-6	652	630	3	-6	379	367	-8	4	182	223
-2	5	747	767	8	5	368	392	-5	-5	165	140	3	-5	484	478	-8	5	245	207
-2	6	150	126	9	-6	303	317	-5	-4	1306	1314	3	-6	687	689	-8	6	216	197
-2	7	181	182	9	-4	621	632	-5	-2	790	811	3	-3	585	614	-7	7	204	258
-2	8	505	510	9	-2	867	841	-5	0	274	287	3	-2	1360	1390	-7	8	422	427
-1	-6	425	398	9	-1	333	328	-5	2	1166	1209	3	-1	907	922	-7	9	498	529
-1	-5	313	340	9	0	1370	1329	-5	3	215	199	3	0	1481	1511	-7	0	741	796
-1	-4	1637	1670	9	1	462	450	-5	4	1168	1162	3	1	1238	1230	-7	1	599	621
-1	-3	706	705	9	2	943	918	-5	5	210	211	3	2	1416	1401	-7	2	590	575
-1	-2	3068	2965	9	3	306	327	-5	6	845	828	3	3	381	367	-7	3	350	353
-1	-1	561	537	9	4	231	247	-5	7	181	198	3	4	391	322	-7	4	323	337
-1	0	1358	1465	10	-7	756	380	-5	8	499	503	3	5	242	231	-7	5	225	207
-1	1	124	103	10	-5	797	816	-4	-8	165	85	3	6	460	439	-7	6	340	330
-1	2	1395	1375	10	-4	243	217	-4	-7	470	478	3	7	272	275	-7	7	483	483
-1	3	213	206	10	-3	823	786	-4	-5	693	667	3	8	421	431	-7	8	469	477
-1	4	197	190	10	-2	225	192	-4	-3	190	182	4	-8	187	212	-6	9	437	458
-1	5	281	282	10	-1	722	708	-4	-1	523	564	4	-7	369	359	-6	10	505	519
-1	6	159	170	10	0	241	222	-4	1	1449	1545	4	-6	705	694	-6	11	678	662
-1	7	722	705	10	1	855	844	-4	2	478	475	4	-5	1128	1150	-6	12	690	681
-1	8	438	427	10	2	333	361	-4	3	2105	2097	4	-4	628	644	-6	13	586	604
0	-6	350	365	10	3	147	160	-4	4	416	399	4	-3	1136	1172	-6	14	278	288
0	-5	1410	1390	11	-7	200	225	-4	5	824	818	4	-2	1072	1068	-6	15	199	186
0	-4	558	580	11	-6	669	688	-4	6	197	176	4	-1	861	904	-6	16	345	350
0	-3	2238	2221	11	-5	316	301	-4	7	392	382	4	0	647	650	-6	17	399	436
0	-2	674	684	11	-4	655	703	-3	-8	486	436	4	1	779	783	-6	18	753	785
0	-1	1286	1219	11	-3	212	232	-3	-6	253	229	4	2	445	430	-6	19	635	667
0	0	606	547	11	-2	213	201	-3	-2	1045	1075	4	3	228	223	-6	20	575	563
0	1	278	260	11	-1	3	170	-3	0	1424	1462	4	4	583	668	-6	21	669	660
0	2	253	242	11	0	520	521	-3	1	539	557	4	5	681	646	-6	22	482	482
0	3	129	114	11	1	5	203	-3	2	2366	2406	4	6	637	633	-6	23	419	427
0	4	749	745	12	-6	244	250	-3	3	549	534	5	-9	199	198	-5	24	392	395
0	5	913	913	12	-5	538	525	-3	4	1019	980	5	-8	389	390	-5	25	431	419
0	6	591	615	12	-4	224	228	-3	5	163	153	5	-7	470	502	-5	26	383	390
1	-8	490	495	12	-3	225	202	-3	6	331	331	5	-6	1013	994	-5	27	527	506
1	-7	213	184	12	-2	255	248	-2	-9	306	273	5	-5	888	888	-5	28	442	443
1	-6	1155	1144	12	-1	233	234	-2	-6	243	233	5	-4	893	895	-5	29	505	477
1	-5	187	189	12	0	607	611	-2	-5	1031	1026	5	-3	723	742	-5	30	762	750
1	-4	1522	1535	12	1	421	425	-2	-4	821	815	5	-2	891	895	-5	31	819	895
1	-3	336	356	12	2	595	588	-2	-3	1421	1407	5	-1	229	242	-5	32	974	1008
1	-2	405	460	12	3	445	245	-2	-2	464	449	5	0	364	381	-5	33	1136	1129
1	0	854	826	13	-5	160	85	-2	-1	1212	1307	5	1	605	627	-5	34	756	759
1	1	1938	1884	13	-2	291	292	-2	0	600	652	5	2	711	713	-5	35	592	566
1	2	170	190	13	-1	262	269	-2	1	1146	1179	5	3	734	759	-5	36	437	427
1	3	1486	1479	13	0	681	654	-2	2	572	575	5	4	548	572	-5	37	625	627
1	4	925	933	13	1	360	358	-2	3	753	762	5	5	406	436	-5	38	397	437
1	5	575	583	13	2	530	525	-2	4	755	741	5	6	291	322	-5	39	337	344
2	-9	691	677	13	3	231	243	-2	5	656	641	6	-8	377	383	-5	40	188	150
2	-7	793	780	14	-3	292	299	-2	6	240	236	6	-7	608	583	-5	41	300	253
2	-5	670	680	14	-2	277	265	-2	7	617	618	6	-6	673	672	-5	42	307	505
2	-2	155	143	14	-1	590	565	-1	-8	243	291	6	-5	748	730	-5	43	280	279
2	-1	325	309	14	0	443	428	-1	-7	229	212	6	-4	481	490	-5	44	351	370
2	0	281	306	14	1	495	497	-1	-6	998	954	6	-3	244	226	-5	45	264	290
2	1	2998	2935	14	2	420	413	-1	-5	721	714	6	-2	336	323	-5	46	686	671
2	2	871	842	14	3	130	163	-1	-4	1910	1905	6	-1	646	637	-5	47	344	389
2	3	1927	2006	14	4	2	130	-1	-3	674	673	6	0	939	928	-5	48	521	522
2	4	197	194	14	5	163	144	-1	-2	1842	1816	6	1	767	846	-5	49	236	247
2	5	1510	1511	14	6	207	198	-1	-1	688	702	6	2	709	763	-5	50	471	459
2	6	463	464	14	7	578	576	-1	0	353	422	6	3	654	641	-5	51	291	262
3	-8	465	447	14	8	185	160	-1	1	232	240	6	4	529	538	-5	52	166	633
3	-6	256	253	14	9	472	449	-1	2	154	115	6	5	506	526	-5	53	290	289
3	-4	385	357	14	10	384	363	-1	3	355	346	6	6	295	333	-5	54	584	580
3	-2	1003	957	14	11	173	162	-1	4	216	220	7	-8	332	340	-5	55	243	188
3	-1	304	286	14	12	640	653	-1	5	1031	1040	7	-7	238	247	-5	56	190	161
3	0	1884	1842	14	13	183	172	-1	6	394	387	7	-6	366	312	-5	57	11	190
3	1	2558	2426	14	14	777	750	-1	7	778	786	7	-5	288	278	-5	58	11	190
3	2	227	211	14	15	326	318	-1	8	300	301	7	-4	253	282	-5	59	0	423
3	3	1310	1314	14	16	659	683	0	-9	351	357	7	-3	531	579	-5	60	216	223
3	4	188	144	14	17	163	131	0	-8	213	173	7	-2	725	741	-5	61	145	110
3	5	181	186	14	18	776	769	0	-7	654	633	7	-1	1035	1035	-5	62	564	569
3	6	306	289	14	19	297	272	0	-6	478	459	7	0	1439	1396	-5	63	262	253
3	7	389	347	14	20	174	162	0	-5	1813	1791	7	1	770	775	-5	64	359	336
3	8	1078	1103	14	21	586	579	0	-4	631	631	7	2	688	644	-5	65	174	187
3	9	1715	1682	14	22	467	479	0	-3	1196	1195	7	3	406	413	-5	66	488	467
3	10	1047	1056	14	23	480	498	0	-2	570	561</								

Table 10 (continued)

K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL	K	L	POBS	PCAL
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	1	824	820	-6	2	645	684	5	2	577	600	-4	-5	256	278	5	3	206	212
3	2	140	104	-6	4	962	968	5	3	465	980	-4	-4	639	614	5	4	451	470
3	3	146	165	-6	6	674	615	5	4	485	980	-4	-3	629	668	6	-7	16	163
3	4	158	150	-5	-7	422	426	5	5	564	549	-4	-2	979	981	6	-5	519	521
3	5	754	736	-5	-3	470	477	5	6	175	149	-4	-1	611	650	6	-4	270	277
3	6	172	170	-5	-1	1155	1204	6	-8	245	257	-4	0	539	551	6	-3	725	765
3	7	643	633	-5	0	181	167	6	-5	201	218	-4	1	242	239	6	-2	312	310
4	-8	572	572	-5	1	1101	1179	6	-4	568	610	-4	4	276	296	6	-1	755	762
4	-6	856	871	-5	3	889	922	6	-3	365	412	-4	5	212	143	6	1	491	500
4	-5	290	293	-5	5	502	486	6	-2	780	839	-4	6	265	254	6	3	266	286
4	1007	1042	-4	-1	618	513	6	-1	631	660	-3	-7	378	406	7	-6	429	461	
4	-3	215	207	-4	-2	1306	1342	6	0	827	791	-3	-6	308	310	7	-5	220	208
4	-2	893	952	-4	0	1644	1671	6	1	472	450	-3	-5	459	433	7	-4	759	828
4	0	396	368	-4	2	714	698	6	2	698	723	-3	-4	502	502	7	-3	209	212
4	2	661	678	-4	4	153	104	6	3	422	434	-3	-3	694	706	7	-2	550	580
4	3	276	262	-3	-7	427	420	6	4	405	407	-3	-2	606	571	7	4	275	307
4	4	998	978	-3	-5	506	526	7	-5	505	554	-3	-1	381	432	8	-5	483	555
4	5	333	310	-3	-3	1280	1281	7	-4	517	575	-3	1	173	108	8	-3	385	425
4	6	987	961	-3	-1	1336	1360	7	-3	833	932	-3	2	397	348	8	1	349	316
5	-8	172	171	-3	1	627	656	7	-2	599	639	-3	3	580	549	8	3	550	555
5	-7	694	673	-3	3	184	151	7	-1	852	856	-3	4	574	566	9	-4	243	258
5	-6	224	236	-3	5	691	661	7	0	382	361	-3	5	563	535	9	0	539	546
5	-5	763	785	-3	7	581	572	7	1	312	305	-3	6	407	393	9	1	182	156
5	-3	243	249	-2	-8	504	520	7	2	200	200	-3	7	352	351	9	2	711	704
5	-1	231	245	-2	-6	748	737	8	-7	171	159	-2	-7	410	396	10	-3	264	255
5	1	525	559	-2	-4	1038	994	8	-6	330	381	-2	-6	438	413	10	-1	562	548
5	2	166	165	-2	-3	188	174	8	-5	417	459	-2	-5	273	296	10	1	658	659
5	3	1212	1248	-2	-2	802	799	8	-4	670	735	-2	-4	324	305	11	-2	533	507
5	4	216	209	-2	0	367	396	8	-3	559	599	-2	-3	302	312	11	0	171	164
5	5	995	1005	-2	2	445	462	8	-2	600	612	-2	0	224	252	11	-2	436	411
5	7	552	572	-2	4	1231	1183	8	-1	331	343	-2	1	554	550	11	-1	178	165
6	-8	544	565	-2	5	163	80	8	0	175	225	-2	2	727	689	11	-1	178	165
6	-6	506	492	-2	6	798	779	8	2	229	199	-2	3	770	726	11	-0	158	144
6	-2	799	878	-1	-7	850	817	8	3	193	197	-2	4	900	856	11	2	200	165
6	0	1031	1045	-1	-5	490	501	8	4	298	306	-2	5	688	658	11	3	183	208
6	2	1247	1357	-1	-3	342	325	8	5	230	255	-2	6	381	394	11	-3	191	184
6	4	663	637	-1	-1	160	172	9	-6	222	232	-2	7	278	283	11	-1	350	356
6	6	584	470	-1	1	403	380	9	-5	324	391	-1	-7	383	346	11	-2	278	254
7	-7	177	165	-1	2	133	115	9	-4	305	358	-1	-6	223	219	11	-3	300	273
7	-5	205	229	-1	3	1366	1326	9	-3	375	388	-1	-3	167	145	11	-4	192	227
7	-3	942	1007	-1	4	171	170	9	1	398	392	-1	-2	286	290	11	-2	210	234
7	-1	1332	1300	-1	5	1118	1097	9	2	446	435	-1	-1	406	403	11	-1	230	209
7	1	1096	1076	-1	6	163	145	9	3	519	524	-1	0	522	573	11	0	495	501
7	3	473	492	-1	7	534	545	9	4	419	423	-1	1	819	801	11	1	296	301
8	-6	308	347	0	-8	603	589	10	-1	314	256	-1	2	794	782	11	2	662	696
8	-4	763	811	0	-6	385	338	10	0	383	391	-1	3	767	756	11	3	513	553
8	-2	1210	1227	0	-4	239	255	10	1	497	490	-1	4	902	868	11	-5	189	220
8	0	892	904	0	-3	359	245	10	2	572	566	-1	5	667	463	11	-3	420	443
8	6	292	330	0	-2	833	803	10	3	554	582	-1	6	292	301	11	-2	259	278
9	-7	353	403	0	-1	253	240	11	-4	208	211	0	-5	258	245	11	-1	650	675
9	-5	611	691	0	0	1133	1097	11	-3	302	274	0	-4	311	339	11	-0	258	257
9	-3	793	817	0	1	221	201	11	-2	389	359	0	-3	694	652	11	1	601	733
9	-1	552	508	0	2	1166	1128	11	-1	456	447	0	-2	619	588	11	2	200	204
9	0	158	38	0	3	346	344	11	0	396	392	0	-1	839	771	11	-6	357	455
9	3	471	475	0	4	953	939	11	1	446	449	0	0	659	638	11	-5	158	162
9	5	581	589	0	5	244	231	11	2	531	536	0	1	832	786	11	-5	197	181
10	-6	478	507	0	6	438	424	12	-3	368	381	0	2	555	540	11	-4	548	554
10	-4	380	364	1	-5	378	362	12	-2	358	361	0	3	547	589	11	-3	221	214
10	-2	205	205	1	-4	250	261	12	-1	358	358	0	4	344	347	11	-2	718	776
10	2	750	754	1	-3	1270	1303	12	0	244	246	0	5	296	299	11	-0	499	515
10	4	686	697	1	-2	349	345	12	1	176	177	0	7	176	177	11	-5	2	275
11	-3	174	175	1	-1	1800	1762	11	-1	535	525	1	-6	338	311	11	-4	165	165
11	-1	409	400	1	0	146	460	11	0	154	146	1	-5	401	368	11	-4	553	626
11	1	692	702	1	1	973	977	11	1	536	529	1	-4	782	776	11	-3	708	669
11	3	622	636	1	2	325	301	11	2	102	130	1	-3	774	764	11	-1	343	397
12	-4	329	342	1	3	699	990	10	-2	620	611	1	-2	891	857	11	0	336	298
12	-2	532	526	1	4	174	177	10	-1	251	252	1	-1	618	601	11	-4	567	441
12	0	616	594	1	5	236	231	10	0	660	643	1	0	590	630	11	-3	6	477
12	2	456	453	1	7	179	170	10	1	208	211	1	1	289	283	11	-3	475	461
12	-3	581	612	2	-6	280	273	10	2	358	346	1	2	303	282	11	-2	219	218
12	-2	192	160	2	-5	187	183	10	4	136	55	1	6	251	271	11	-3	0	382
13	-1	489	506	2	-4	1203	1188	9	-3	458	485	2	-7	417	384	11	-3	2	693
13	0	130	108	2	-3	397	408	9	-2	269	247	2	-6	344	332	11	-3	655	634
13	2	173	168	2	-2	1513	1529	9	-1	662	613	2	-5	712	602	11	-2	5	128
13	4	173	168	2	-1	484	492	9	0	242	231	2	-4	651	617	11	-1	476	468
13	6	253	252	2	0	1210	1295	9	1	325	305	2	-3	934	951	11	-2	1073	1020
13	-1	304	297	2	2	309	304	9	5	341	352	2	-2	536	499	11	-2	2	190
13	0	212	225	2	4	359	327	8	-5	196	141	2	-1	516	517	11	-2	3	883
13	1	523	517	2	6	379	372	8	-4	346	342	2	1	226	225	11	-2	5	506
13	2	250	234	2	7	243	214	8	-2	409	402	2	2	272	242	11	-1	4	267
13	3	482	485	3	-7	512	501	8	0	181	142	2	3	481	454	11	-2	753	712
13	4	199	206	3	-5	690	703	8	-2	260									

TABLE 11: FRACTIONAL COORDINATES

Atom	x	y	z
Re1	0.02212 (8)	0.16212 (5)	0.20948 (7)
Re2	0.19138 (8)	0.35578 (5)	0.29300 (7)
Si1	0.2768 (5)	0.1950 (3)	0.3623 (5)
Si2	-0.0608 (5)	0.3230 (3)	0.1359 (5)
C1	0.143 (2)	0.141 (1)	0.040 (2)
C2	-0.166 (2)	0.123 (1)	0.093 (2)
C3	0.054 (2)	0.037 (1)	0.266 (2)
C4	-0.092 (2)	0.187 (1)	0.381 (2)
C5	0.309 (2)	0.342 (1)	0.117 (2)
C6	0.303 (2)	0.479 (2)	0.351 (2)
C7	0.078 (2)	0.378 (1)	0.470 (2)
C8	0.460 (2)	0.147 (1)	0.284 (2)
C9	0.273 (2)	0.172 (1)	0.560 (2)
C10	0.479 (2)	0.040 (1)	0.287 (2)
C11	0.426 (2)	0.216 (2)	0.650 (2)
C12	-0.057 (2)	0.342 (1)	-0.061 (2)
C13	-0.242 (2)	0.369 (1)	0.208 (2)
C14	-0.198 (2)	0.292 (2)	-0.157 (2)
C15	-0.288 (2)	0.469 (2)	0.169 (2)
O1	0.212 (2)	0.130 (1)	-0.059 (1)
O2	-0.281 (2)	0.097 (1)	0.027 (1)
O3	0.081 (2)	-0.041 (1)	0.293 (2)
O4	-0.164 (2)	0.199 (1)	0.482 (1)
O5	0.378 (1)	0.336 (1)	0.019 (1)
O6	0.362 (2)	0.550 (1)	0.393 (2)
O7	0.015 (2)	0.394 (1)	0.574 (1)

TABLE 12: THERMAL PARAMETERS (\AA^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B(\text{\AA}^2)_a$
Re1	0.0497(5)	0.0456(5)	0.0432(5)	-0.0010(4)	-0.0004(3)	0.0031(4)	3.67
Re2	0.0448(5)	0.0436(5)	0.0483(4)	0.0010(4)	-0.0038(4)	0.0039(4)	3.63
Si1	0.0585(30)	0.0501(26)	0.0519(26)	0.0069(23)	-0.0042(21)	0.0098(21)	4.22
Si2	0.0512(28)	0.0553(27)	0.0483(25)	-0.0024(23)	-0.0051(21)	0.0101(21)	4.09
C1	0.070(13)	0.058(11)	0.071(14)	0.003(10)	0.014(11)	-0.013(11)	5.33
C2	0.076(13)	0.056(10)	0.040(10)	-0.017(9)	0.005(9)	-0.012(8)	4.68
C3	0.087(14)	0.053(11)	0.051(11)	-0.017(10)	-0.020(10)	0.008(9)	5.13
C4	0.055(12)	0.060(11)	0.059(13)	0.009(9)	0.006(10)	0.001(10)	4.58
C5	0.050(10)	0.054(10)	0.051(9)	-0.008(8)	-0.005(8)	0.014(8)	4.08
C6	0.038(10)	0.096(15)	0.067(12)	0.001(10)	-0.014(8)	0.001(11)	5.39
C7	0.074(12)	0.051(11)	0.052(10)	0.003(9)	-0.001(9)	0.006(8)	4.68
C8	0.057(12)	0.075(12)	0.082(14)	0.021(10)	0.012(10)	0.019(10)	5.50
C9	0.083(13)	0.077(12)	0.044(10)	-0.004(11)	-0.010(9)	0.015(9)	5.40

TABLE 12 CONTINUED

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B(\text{\AA}^2)^a$
C10	0.091(15)	0.065(13)	0.111(15)	0.027(11)	0.011(12)	0.025(12)	6.88
C11	0.092(15)	0.111(17)	0.069(13)	-0.014(13)	-0.033(11)	0.019(12)	7.28
C12	0.091(14)	0.067(12)	0.049(10)	-0.012(11)	-0.003(9)	0.008(8)	5.50
C13	0.054(11)	0.065(12)	0.089(13)	0.011(9)	0.000(9)	0.008(10)	5.48
C14	0.095(15)	0.101(15)	0.057(11)	-0.026(13)	-0.023(10)	0.019(11)	6.75
C15	0.066(13)	0.060(12)	0.115(16)	0.021(10)	0.004(11)	-0.000(11)	6.38
O1	0.111(12)	0.099(11)	0.074(10)	-0.009(9)	0.033(9)	-0.012(8)	7.52
O2	0.084(10)	0.093(10)	0.074(9)	-0.015(9)	-0.009(8)	-0.011(8)	6.79
O3	0.124(13)	0.063(9)	0.120(11)	0.007(9)	-0.006(9)	0.021(8)	8.06
O4	0.089(11)	0.107(11)	0.060(9)	-0.013(9)	0.008(8)	0.011(8)	6.75
O5	0.070(9)	0.101(10)	0.078(9)	0.007(8)	0.021(7)	0.010(8)	6.48
O6	0.087(11)	0.069(9)	0.124(12)	-0.020(8)	-0.024(9)	-0.002(9)	7.61
O7	0.108(11)	0.085(10)	0.076(9)	0.012(9)	0.031(8)	-0.018(7)	7.15

^aEquivalent isotropic thermal parameter.

TABLE 13: INTRAMOLECULAR DISTANCES^a (Å)

Atoms	Distance	Atoms	Distance
Re1-Re2	3.052(1)	Re2-Si1	2.539(4)
Re1-Si1	2.547(5)	Re2-Si2	2.549(4)
Re1-Si2	2.548(5)	Re1-C1	1.96(2)
Re1-C2	1.93(2)	Re1-C3	1.92(2)
Re1-C4	1.94(2)	Re2-C5	1.98(2)
Re2-C6	1.97(2)	Re2-C7	1.98(2)
C1-O1	1.13(2)	C2-O2	1.15(2)
C3-O3	1.18(2)	C4-O4	1.16(2)
C5-O5	1.12(2)	C6-O6	1.12(2)
C7-O7	1.15(2)	Si1-C8	1.90(2)
Si1-C9	1.91(2)	Si2-C12	1.89(2)
Si2-C13	1.85(2)	C9-C11	1.59(2)
C8-C10	1.53(2)	C12-C14	1.56(2)
C13-C15	1.54(2)		

^aStandard deviations in parentheses refer to last digit quoted.

TABLE 14: INTRAMOLECULAR ANGLES (DEGREES)

Atoms	Angle	Atoms	Angle
Sil-Re2-Re1	53.3(1)	Sil-Re1-Re2	53.0(1)
Si2-Re2-Re1	53.2(1)	Si2-Re1-Re2	53.2(1)
Re2-Sil-Re1	73.7(1)	Re2-Si2-Re1	73.5(1)
Sil-Re1-C3	80.4(5)	Si2-Re1-C2	79.8(5)
Re2-Re1-C1	89.7(5)	Re2-Re1-C4	88.2(5)
Re1-Re2-C5	92.4(5)	Re1-Re2-C6	178.6(5)
Re1-Re2-C7	91.1(5)	Re1-C1-O1	179(2)
Re1-C2-O2	178(2)	Re1-C3-O3	175(2)
Re1-C4-O4	178(2)	Re2-C5-O5	178(2)
Re2-C6-O6	175(2)	Re2-C7-O7	178(2)
C8-Sil-C9	110.4(8)	C12-Si2-C13	109.6(8)
C10-C8-Sil	115(1)	C11-C9-Sil	110(1)
C14-C12-Si2	114(1)	C15-C13-Si2	116(1)
Sil-Re2-C6	125.5(5)	Si2-Re2-C6	128.0(5)

TABLE 15: LEAST SQUARES PLANE CALCULATIONS ^aFOR $\text{Re}_2(\text{CO})_7\text{H}_2(\text{SiEt}_2)_2$

(A) ATOMS DEFINING PLANE: Re1, Re2, Si1, Si2

EQUATION OF PLANE:

$$-0.5693X + 0.0653Y + 0.8195Z - 1.6898 = 0.0$$

DISTANCES OF ATOMS FROM PLANE: Re1 0.0029

Re2 0.0031

Si1	-0.020	Si2	-0.020
C6	0.026	O6	0.127
C2	-0.017	O2	0.002
C3	0.179	O3	0.184
C5	-1.980		

(B) ATOMS DEFINING PLANE: Re1, Re2, C1, C4, C5, C7.

EQUATION OF PLANE:

$$0.6782X - 0.5229Y + 0.5163Z + 0.0354 = 0.0$$

DISTANCES OF ATOMS FROM PLANE:

Re1	0.0004	Re2	0.0004
C1	0.049	C4	-0.029
C5	-0.049	C7	0.016
O1	0.065	O4	-0.055
O5	-0.077	O7	0.038
C6	0.043	O6	0.089
Si1	-2.041		

^aX, Y, and Z are orthogonal coordinates (Å) with X along the *a*-axis, Y in the (*a*, *b*) plane, and Z along the *c*^{*}-axis.

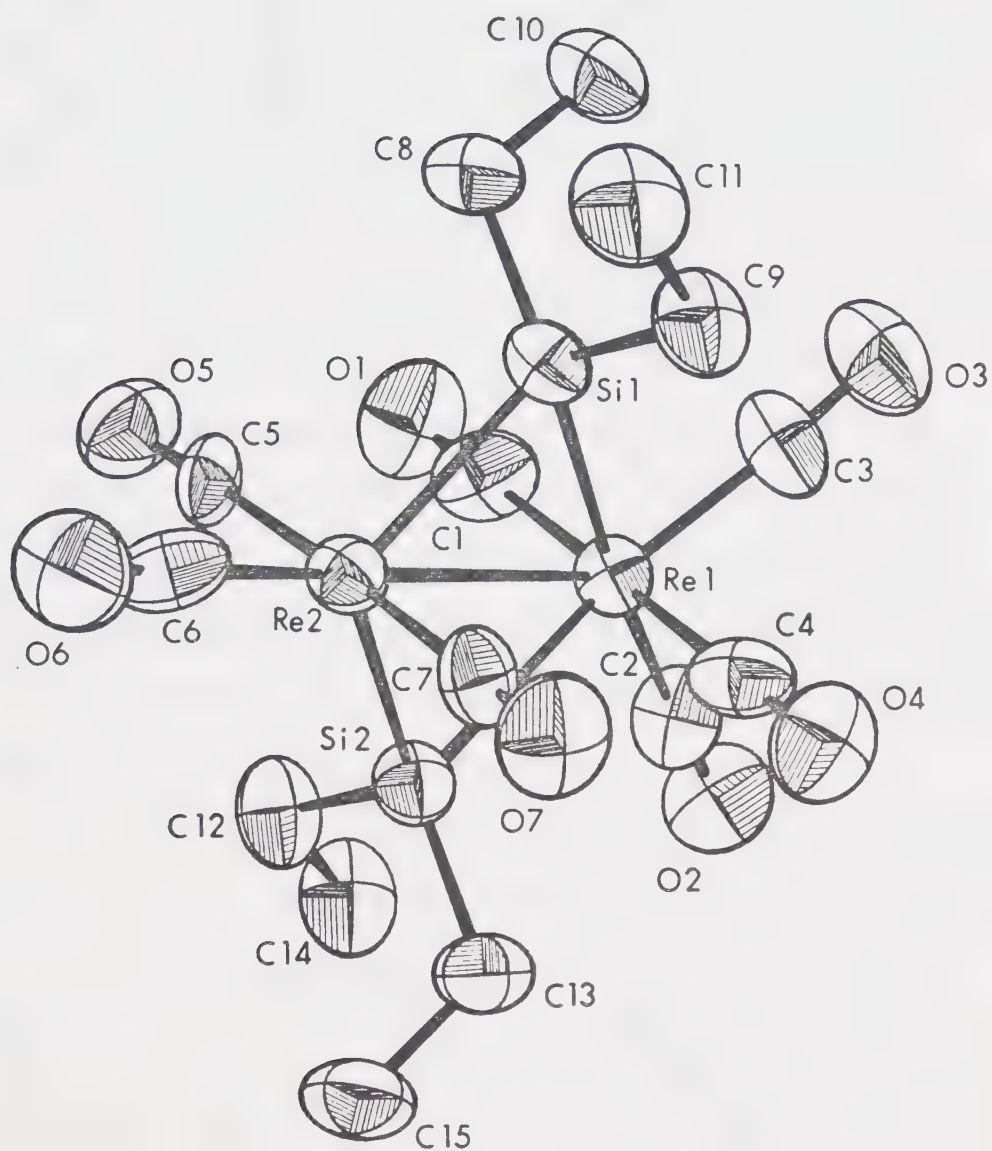


Fig. 5: A PERSPECTIVE VIEW OF $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$.

DESCRIPTION OF STRUCTURE

$\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ has approximate C_s symmetry. A perspective view of the molecule is shown in Fig. 5. The central cluster is similar to that of $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ shown in Chapter II. The two rhenium atoms and two silicon atoms are planar and located at the corners of a rhombus, with like atoms at opposing corners, and a rhenium-rhenium bond across the shorter diagonal. Two carbonyl groups (C303 and C202) on Re1 are also approximately in this plane and *trans* to the Re1-Si1 and Re1-Si2 bonds, while one carbonyl group (C606), also in this plane and bonded to Re2, lies along the Re-Re bond. The two remaining carbonyls on each rhenium are perpendicular to the Re_2Si_2 plane above and below the rhenium atoms.

The rhenium-carbon (carbonyl) and carbon-oxygen distances are regular and similar to those observed in $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ and other rhenium carbonyl compounds.^{64,65,82,83,87,88,89} The coordination around the silicon atoms is a distorted tetrahedron due to the small Re1-Si-Re2 angles. There are no unusual distances in the silicon-carbon (ethyl) or carbon-carbon (ethyl) bonds (compare Chapter II). The rhenium-rhenium distance [$3.052(1) \text{ \AA}$] is consistent with a rhenium-rhenium single bond, and this is further

substantiated by the acute Re1-Si1-Re2 and Re1-Si2-Re2 angles of $73.7(1)^\circ$ and $73.5(1)^\circ$. It is also interesting that there is a progression in Re-Re bond lengths through the series $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$,⁶⁴ $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$, $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ and $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$,⁶⁵ whereas the Re-Si bonds are approximately constant (Table 16).

The longer Re-Re bond in $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$ reflects the fact that only one Si bridge is constraining the rhenium atoms together and also that the two extra eclipsed carbonyls are present causing added repulsion of the two $\text{Re}(\text{CO})_4$ moieties. It is believed however that the Re-Re bond length differences in the other three compounds indicate that there is significant π bonding present in the Re-Re bonds whereas the Re-Si bonds are primarily σ . Thus varying the number of π -withdrawing carbonyl groups in the molecules would be expected to affect the Re-Re bonds if π bonding is important, but have little effect on the Re-Si bonds if the π bonding contribution here is not great.

Using the covalent radii of Pauling²⁷ for Si (1.17 \AA) and Re (1.283 \AA) a single bonded Re-Si distance of 2.45 \AA is predicted, which is less than the observed value of approximately 2.54 \AA in these

compounds (Table 16). Although the radius used for rhenium may not be suitable, the larger observed Re-Si bond length does not weaken the argument that rhenium-silicon π bonding is of little significance in these compounds. A similar trend was observed⁹⁰ in $\text{Cl}(\pi\text{C}_5\text{H}_5)_2\text{ZrSi}(\overset{\circ}{\text{C}}_6\text{H}_5)_3$ where the observed Zr-Si distance [2.813(2) Å] exceeded the value calculated with Pauling radii (2.62 Å). Here Zr(IV) is formally d^0 so no back-donation into empty silicon d orbitals can occur. Thus it was postulated that only σ bonding was important. This contrasts with $\text{Co}(\text{SiCl}_3)(\text{CO})_4$ ⁹¹ and $\text{RhHCl}(\text{SiCl}_3)(\text{PPh}_3)_2$ ⁹² where the Co-Si [2.254(3) Å] and Rh-Si [2.303(4) Å] distances are both less than the values predicted using Pauling's covalent radii (2.33 Å and 2.42 Å respectively). It seems therefore that metal-silicon π bonding is present in these two compounds, whereas it is minimal in the zirconium and rhenium compounds. Any explanation of bond shortening as due to π bonding in these transition metal silyl compounds should be approached cautiously, however, since it is difficult to separate these effects from a σ -inductive effect. Thus the changes in metal-silicon distances in the series $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{HMnSi}(\overset{\circ}{\text{C}}_6\text{H}_5)_3$ ⁹³ [2.424(2) Å]; $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{HMnSiCl}_2(\overset{\circ}{\text{C}}_6\text{H}_5)$ ⁹⁴ [2.310(2) Å]; and also

the series $\text{Co}(\text{SiH}_3)(\text{CO})_4$,⁹⁵ [2.381(7) Å]; $\text{Co}(\text{SiCl}_3)(\text{CO})_4$,⁹¹ [2.254(3) Å]; and $\text{Co}(\text{SiF}_3)(\text{CO})_4$,⁹⁶ [2.226(5) Å]; can be attributed to shrinkage of the silicon orbitals by the more electronegative substituents, thereby shortening the metal-silicon bonds.

However uncertain the mode of bonding between the rhenium and silicon atoms, it is still possible to compare the distances within the series mentioned in Chapter II since all substituents are similar. Thus the most interesting feature of $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ is the similarity in the Re-Si bond lengths and their similarity to the other members of the series. The Re2-Si1 and Re2-Si2 bonds are adjacent to the hydrogen ligands whereas the Re1-Si1 and Re1-Si2 bonds are "hydrogen-free". As was explained in Chapter II, the similarity of these bonds in the two differing environments is not expected in view of the proposed hydrogen bridging.^{62,63} Again, complete discussion of this phenomenon is deferred until Chapter IV.

CHAPTER IV: MODE OF BONDING OF THE HYDRIDE

LIGANDS IN $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$

AND $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$

Although location of the hydrogen atoms in this series of hydrides was not possible due to high dominance of the rhenium and tungsten scattering and also large absorption effects, investigation of the central framework, in particular the transition metal-silicon bond, has proved exceedingly valuable in obtaining information about the bonding exhibited by the hydrogens attached to the metals.⁶⁶ Three possibilities exist for the hydrogen bonding in these compounds as shown for $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ in Fig. 6: (1) the hydrogen is terminally bonded to the transition metal with no interaction with the silicon, (2) the hydrogen bridges the transition metal-silicon bond thus forming a three centre two electron bond, and (3) the hydrogen is terminally bonded to the transition metal, but with weak attractive interaction with the silicon. A hydrogen bridge of type (2) was postulated⁶⁶ for $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ in which the W-Si distances differed significantly (Table 16), with the hydrogen presumably bridging the longer distance. However,

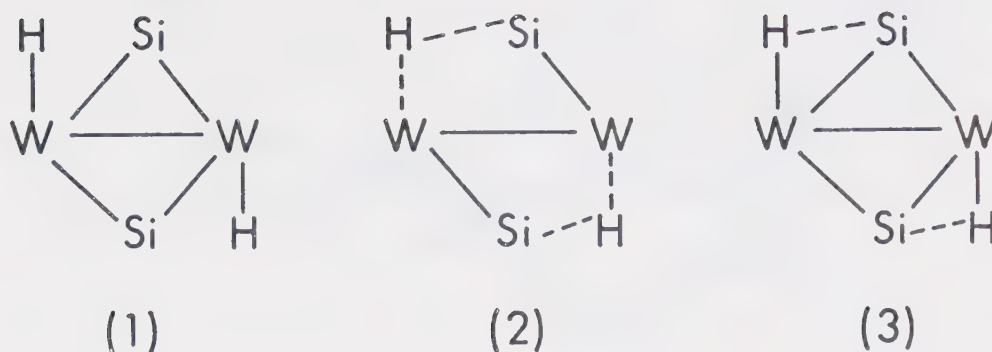


Fig. 6: Possible Bonding Schemes for the Hydrogen Ligand in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$.

in $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ the Re-Si bond lengths are not consistent with a three centre Si-H-Re bond, but rather seem consistent with a terminally bound hydrogen ligand.

It was expected that if the hydrogen was involved in a three centre Si-H-Re bond, a significant lengthening of this Si-Re distance would be observed, analogous to $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$. There is no significant difference in Re-Si bond lengths, however, between the two hydrides $Re_2(CO)_8H_2Si(C_6H_5)_2$ ⁶⁵ and $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$, and $Re_2(CO)_8[Si(C_6H_5)_2]_2$ ⁶⁴ which contains no hydrogen ligand. Moreover these Re-Si distances are similar to the shorter (unbridged) W-Si distance in $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$, and therefore

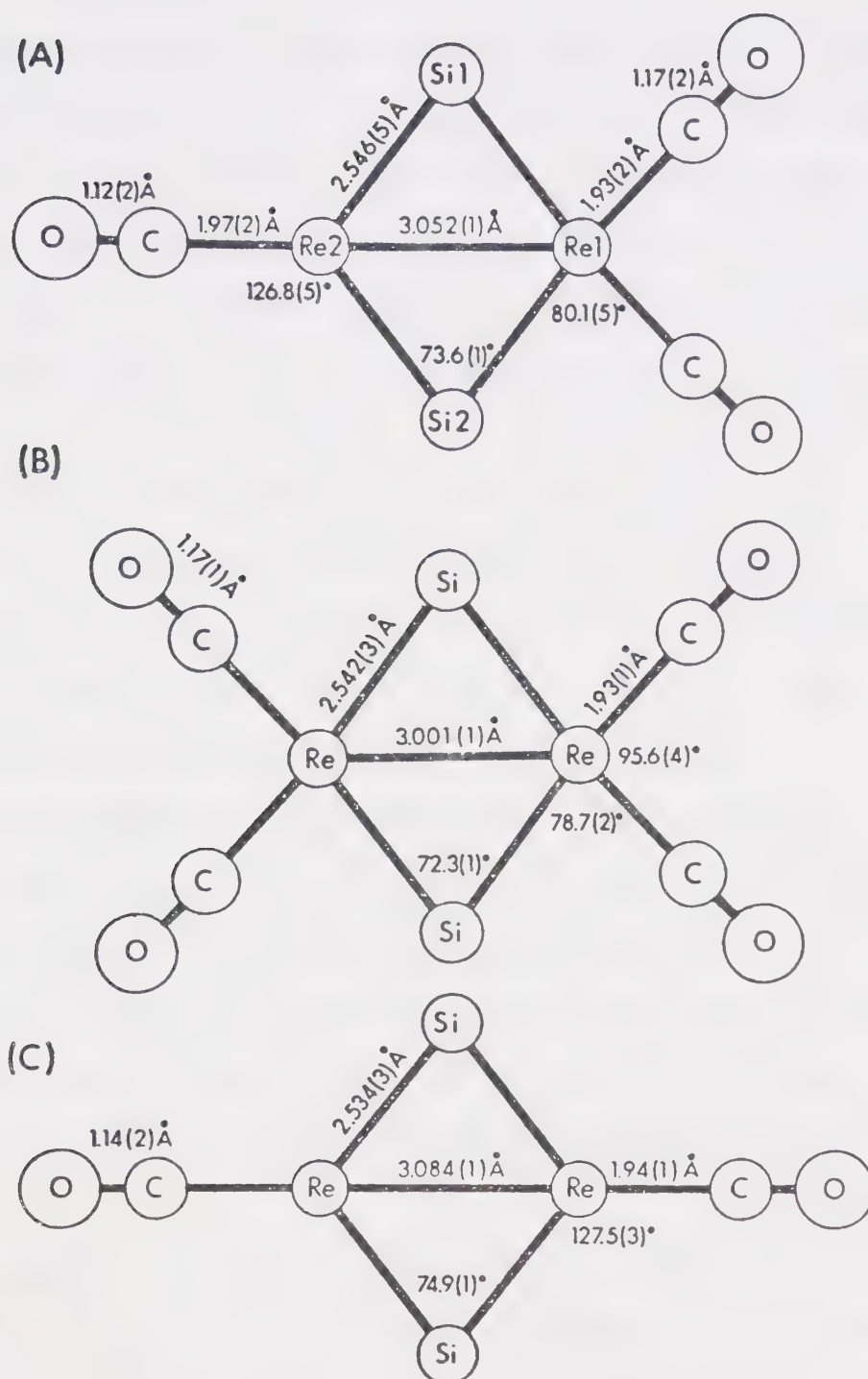


Fig. 7: A COMPARISON OF THE GEOMETRIES OF
 (A) $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$, (B) $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$, AND
 (C) $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$.

are more consistent with terminal hydrides.

The ambiguity in comparison of the Re-Si bond lengths in the hydrides and $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$, in which the disorder problem existed (Appendix 1), was overcome with the structural determination of $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$, which, like the tungsten complex, was an internal standard containing metal-silicon bonds both adjacent to hydrogen ligands and "hydrogen-free". The similarity of the Re-Si bonds in this structure was added proof that the hydrogen ligands were not bonded in a fashion analogous to $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ and were therefore probably bound terminally to the rhenium atom. This reinforced the previous argument that the other rhenium hydrides in this series were also terminal.

Fig. 7 shows $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$, $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ and $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ viewed perpendicular to the Re_2Si_2 planes and including only those atoms lying approximately in this plane. Included are relevant bond lengths and angles for ready comparison of the three.

To explain why the hydrogen ligands seem to be terminally bound for the rhenium compounds, but bridging in the case of the tungsten compound, it is useful to consider the coordination about the metal atoms, as shown in Fig. 8. In each compound there are two mutually *trans* carbonyl groups on each metal which are not shown. These are perpendicular to the

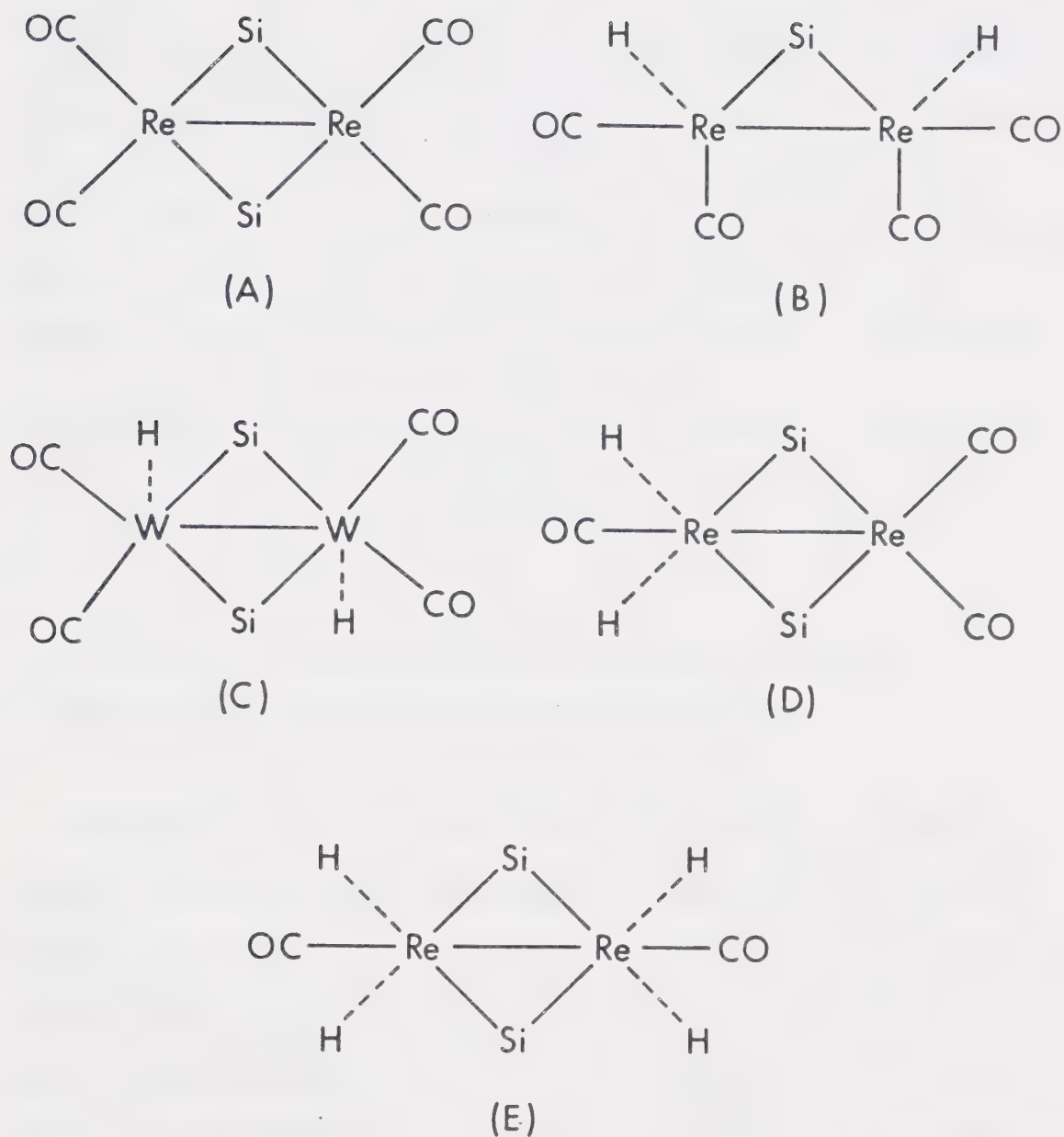


Fig. 8: HYDROGEN LIGAND ENVIRONMENTS IN THE SILICON BRIDGED TRANSITION METAL HYDRIDES.

TABLE 16: RELEVANT BOND LENGTHS (Å)

IN SOME TRANSITION METAL SILICON-BRIDGED COMPLEXES

COMPOUND	M-Si	M-M	REFERENCE
$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$	2.586(5), 2.703(4)	3.183(1)	66
$Re_2(CO)_8H_2Si(C_6H_5)_2$	2.544(9)	3.121(2)	65
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	2.542(3)	3.001(1)	64
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	2.533(2), 2.535(3)	3.084(1)	THIS WORK
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	2.547(5), 2.548(5), 2.539(4), 2.549(4)	3.052(1)	THIS WORK

TABLE 17: RELEVANT ANGLES (DEGREES) IN SOME
TRANSITION METAL SILICON-BRIDGED COMPLEXES

COMPOUND	Si-M-M	M-Si-M	Si-M-C
$W_2(CO)_8H_2[Si(C_2H_5)_2]_2$	53.02(10)	73.97(12)	109.1(5)
$Re_2(CO)_8H_2Si(C_6H_5)_2$	53.9(1)	72.3(1)	124.8(13)
$Re_2(CO)_8[Si(C_6H_5)_2]_2$	52.2(2)	75.7(3)	78.7(2)
$Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$	52.6(1)	74.9(1)	127.5(3)
$Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$	53.2(1)	73.6(1)	126.8(5)

plane of the central cluster and are a constant feature of all the structures. Hydrogen atoms, although not located experimentally, are positioned in what are thought to be their approximate locations.

Viewing the hydrogen ligand environments in the examples shown, it is obvious that in the tungsten hydride (C), the hydrogen is more crowded than in the rhenium hydrides. The Si-W-C (carbonyl) angle, which encloses the hydrogen ligand is $109.1(5)^\circ$ in the tungsten hydride, compared to the analogous angles of $124.8(13)^\circ$, $126.8(5)^\circ$, and $127.5(3)^\circ$ in the rhenium hydrides (B), (D), and (E) respectively. It has been shown^{93,94,97} that a normal non-bonded H-C (carbonyl) contact can be as low as 2.0 \AA . For a Re-H distance²⁹ of 1.68 \AA calculations show that in the rhenium hydrides, maintaining the minimum C-H contact, a H-Si contact of greater than 2.2 \AA arises. However the situation is much different for $\text{W}_2(\text{CO})_8\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$. If no hydrogen bridging concept is utilized, then using the unbridged W-Si distance of 2.586 \AA , and maintaining the minimum C-H contact, a very short Si-H contact of 1.72 \AA occurs (this calculated assuming a W-H distance⁹⁸ of 1.70 \AA). Even using the larger W-Si distance, a short Si-H contact of 1.81 \AA arises. Therefore the hydrogen

ligands are constrained to be considerably closer to the silicon atoms in the tungsten compound. It is believed that the crowding of the hydrogen by the carbonyl group is then responsible for the appearance of the three centre W-H-Si bond, since it is possible that the three centre bond is favoured energetically over a terminal hydride involving the high repulsion energy which must be associated with the very short Si-H non-bonded contacts mentioned.

The non-bonded Si-H contact of 2.2 \AA calculated for the rhenium hydrides is believed to be reasonable. In $(\pi\text{-C}_5\text{H}_5)(\text{CO})\text{HFe}(\text{SiF}_3)_2$ the hydrogen was not believed⁹⁹ bonded to either silicon atom and was located at $2.06(7) \text{ \AA}$ from both silicons. Although seemingly short, these non-bonded contacts can occur because in these systems the hydrogens approach the silicon atoms in electron density nodes, for example between the F-Si-F covalent bonds in $(\pi\text{-C}_5\text{H}_5)(\text{CO})\text{HFe}(\text{SiF}_3)_2$, or between the C-Si-C bonds in the rhenium hydrides discussed. The repulsion is minimized in these bonding nodes thus facilitating the approach of the hydrogen ligand to the silicon atom.

There seems therefore to be no inherent stability of the hydrogen-bridged metal-silicon bond. Rather, the three centre bond is the result of steric crowding

by an adjacent carbonyl group and only appears, as for $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$, when the hydrogen ligand is restricted to be close to the silicon atom.

Although evidence obtained from the structural investigations of $Re_2(CO)_6H_4[Si(C_2H_5)_2]_2$ and $Re_2(CO)_7H_2[Si(C_2H_5)_2]_2$ combined with that obtained from^{64,66} $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$ and $Re(CO)_8[Si(C_2H_5)_2]_2$ exclude the possibility of a three centre Re-H-Si bond, it does not exclude the existence of weak attractive interaction of the hydrogen ligand with the silicon atom. An insight into this possibility is gained from the structural investigations^{93,94,97} of $(\pi-C_5H_5)(CO)_2HMnSi(C_6H_5)_3$, $(\pi-C_5H_5)(CO)_2HMnSiCl_2(C_6H_5)$ and $(CO)_4FeHSi(C_6H_5)_3$, in which the hydrogen ligands were located experimentally. In both manganese compounds the hydrogens were located at $1.55(4) \text{ \AA}$ and $1.49(6) \text{ \AA}$ respectively from the manganese atoms and $1.76(4) \text{ \AA}$ and $1.79(6) \text{ \AA}$ respectively from the silicon atoms. However, in the iron compound the hydrogen atom was $1.64(10) \text{ \AA}$ from the iron atom and $2.73(10) \text{ \AA}$ from the silicon atom. In the two manganese hydrides the hydrogen ligands are constrained to be close to the silicon atoms due to steric crowding, the hydrogen being only $2.08(4) \text{ \AA}$ from the carbonyl in $(\pi-C_5H_5)(CO)_2HMnSi(C_6H_5)_3$ and $1.98(6) \text{ \AA}$ from the carbonyl

in $(\pi\text{-C}_5\text{H}_5)(\text{CO})_2\text{HMnSiCl}_2(\text{C}_6\text{H}_5)$. There is no possibility of increasing the H-Si distance without increasing the hydrogen contact with the carbonyl groups. However in $(\text{CO})_4\text{FeHSi}(\text{C}_6\text{H}_5)_3$ the hydrogen is not constrained to be close to the silicon atom, since it is in a sterically less crowded environment than the manganese hydrides. Thus the long Si-H contact observed is indicative of a terminally bound hydrogen with no attraction to the silicon atom. This is interpreted as meaning that there is no inherent stability of the weakly bridged hydrogen in this series in preference to a simple terminal hydrogen.

Thus in conclusion, in this series of transition metal hydrides, the hydrogen atoms are bound terminally to the transition metals in all the rhenium complexes. The hydrogens only approach the silicon atoms, as in the tungsten and manganese complexes, as a result of steric crowding and not as a result of any unusual attraction to the silicon atoms.

CHAPTER V: DITHIOLENE¹⁰⁰ INTRODUCTION

Interest in the bidentate dithiolene ligands began in the mid 1930's when R. E. D. Clark discovered^{101,102} that toluene-3,4-dithiol and 1-chlorobenzene-3,4-dithiol reacted with zinc, cadmium, mercury and tin halides to form complexes of the type $[M(\text{dithiol})_2]$. This reaction was found to be especially effective in the analytical determination of tin^{103,104} and of molybdenum and tungsten^{105,106,107} and most attention was directed towards this end. By the early 1960's several dithiolene complexes had been characterized^{108,109,110} and were found to be of the form $M(\text{dithiol})_2$ involving a variety of dithiolene ligands combined with nickel, cobalt, palladium, and molybdenum. These *bis* dithiol complexes were found to possess two unusual properties. Firstly, they exhibited the unusual square planar geometry^{111,112,113,114} with the sulfur atoms in an almost perfect square about the metal. And secondly, they underwent facile reversible oxidation-reduction reactions¹¹⁵ without changes in coordination geometry. The oxidized and reduced species were found to be related simply by one electron transfers and could be detected using polarography and voltammetry.

Attempts to produce the *bis* complexes of $S_2C_2Ph_2$ with V, Cr, Mo, Re, W, Ru, and Os¹¹⁶ instead yielded

the six coordinate *tris* complexes^{117,118,119} which were similar to the *bis* complexes in that they also underwent the facile oxidation-reduction reactions.^{119,120,121} The discovery¹²² that $\text{Co}[\text{S}_2\text{C}_2(\text{CN})_2]_2^-$ reversibly added one mole of ligand to form the complex $\text{Co}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{3-}$ led to the interesting suggestion that the six coordinate cobalt complex and possibly even the other *tris* complexes could be trigonal prismatic. In addition doubt about the octahedral coordination of these complexes was raised because of the inability to separate $\text{Co}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{3-}$ and $\text{Mo}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_3$ into their optical enantiomers.¹²³ The possibility of trigonal prismatic coordination was extremely unusual since no six coordinate molecular complexes had been observed with non-octahedral coordination. Trigonal prismatic coordination *had* been observed¹²⁵ as early as 1923 in the compounds MoS_2 and WS_2 and later¹²⁶ in NiAs . However these were infinitely extended lattices and molecular packing was believed responsible for their unusual coordination.¹²⁴ It is noteworthy that on the basis of "directed valence" calculations, it had even been predicted by Hultgren¹²⁷ in 1932, that the only stable six coordinate complexes were trigonal prismatic and octahedral, the former being preferred for low lying d orbitals and the latter being preferred

for higher energy d orbitals. In addition octahedral coordination would be favoured by increasing ionic character in the metal-ligand bonds and by the bulkiness of large ligands.

The existence of trigonal prismatic coordination in a molecular complex was not observed until 1965 when the X-ray structure determination^{128,129} of $\text{Re}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_3$ was completed. The subsequent structural determinations of $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ ¹³⁰ and $\text{V}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_3$ ^{131,132} also showed trigonal prismatic geometry and verified that the rhenium compound was not an isolated example but only one of a possible series of trigonal prismatic structures. In all three compounds the metals were surrounded by six sulfur atoms at the corners of a trigonal prism, with the dithiolene ligands radiating from the metals in a "paddle-wheel" arrangement. There was also a striking similarity in the prism dimensions of the three compounds (Table 48). The intra- and interligand sulfur-sulfur distances are similar in all cases with the approximate values 3.06 Å and 3.08 Å respectively. The shortness of these "non-bonded" contacts led to the speculation that some sulfur-sulfur bonding was involved¹²⁴ in stabilizing the trigonal prism. Another remarkable feature of the three complexes was

the similarity in the metal-sulfur bond lengths, averaging 2.33 \AA , despite the fact that the covalent and ionic radii¹³³ of vanadium differed from those of molybdenum and rhenium by 0.07 \AA . This similarity was viewed as an added consequence of the interligand S-S bonding.¹²⁴ In addition the S-C distances, averaging 1.69 \AA were found to be consistent with considerable double bond character as seen from a comparison with the S=C double bond in thiourea¹³⁴ $[\text{SC}(\text{NH}_2)_2]$ and its derivatives,¹³⁵ measuring 1.720 \AA .

Slight differences are, however, present in the three compounds which lead to distortions from the idealized D_{3h} symmetry. $\text{Re}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_3$ and $\text{Mo}[\text{S}_2\text{C}_2(\text{CN})_2]_3$ both have approximate C_{3h} symmetry caused by twisting of the phenyl groups out of the ligand planes in the former and by a deviation of the S_2C_2 planes from the MS_2 planes by 18° in the latter. In $\text{V}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_3$ the unique ligand on the crystallographic two-fold differs slightly from the other two, however the molecule still closely approximates D_{3h} symmetry.

Comparison of the electron spin resonance and electronic spectra in the solid state and in solution¹³⁶ confirmed that the trigonal prismatic coordination was also present in solution and therefore was a

consequence of intramolecular phenomena rather than intermolecular effects. It was also apparent in all the electronic spectra that the dominant feature was an intense two-band pattern in the visible region,¹³⁷ the first at about $15,000 \text{ cm}^{-1}$ ($\epsilon \sim 25000$) and the second at about $24,000 \text{ cm}^{-1}$ ($\epsilon \sim 15000$). This was believed to be characteristic of all trigonal prismatic dithiolenes.

In an attempt to explain the stability of the trigonal prism over the octahedron, two separate molecular orbital treatments were presented. In the treatment by Schrauzer and Mayweg¹³⁸ no reason for the stability of the trigonal prism is obvious since calculations performed on a hypothetical octahedral complex $\text{MS}_6\text{C}_6\text{R}_6$ yielded the same orbital ordering as the trigonal prismatic calculations. Also objections based on electron spin resonance spectra have been raised¹³⁹ concerning the ordering of the highest occupied and lowest unoccupied levels for this scheme. The scheme by Gray *et. al.*,¹³⁷ which seems more consistent with electron spin resonance spectra, electronic spectra and polarographic work is therefore favoured in this work. Both schemes are discussed further in Chapter IX where a detailed explanation of the trigonal prism is given based on

Gray's molecular orbital calculations.

Although the neutral *tris* dithiolenes were found to be trigonal prismatic, subsequent structural determinations on $\text{V}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$,¹⁴² $\text{Mo}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$,¹⁴¹ and $\text{Fe}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$ ¹⁴² showed coordinations which varied from highly distorted octahedrons for the vanadium and molybdenum dianions to an almost regular octahedral coordination for the iron dianion. Interligand sulfur-sulfur distances in the three were greater than for the neutral trigonal prisms and thus were consistent with a breakdown in the sulfur-sulfur bonding which had been proposed¹²⁴ as a stabilizing factor in the prism. In addition the extra electrons in the molybdenum dianion as compared to the neutral molybdenum complex were located in an orbital which was said to be antibonding in the trigonal prism¹⁴¹ thus offering an explanation of the deviation from the trigonal prismatic coordination. The trend therefore emerged that the neutral *tris* 1,2-dithiolenes were trigonal prismatic whereas the dianions were octahedral or distorted octahedral. The reasons for the trigonal prismatic and octahedral coordination in these dithiolenes was not obvious however and little was published correlating the observed structures to the molecular orbital descriptions of either Gray or

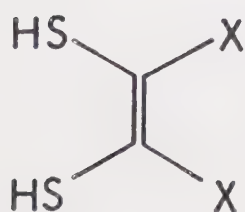
Schrauzer.

The compounds $\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$, $[(\text{C}_6\text{H}_5)_4\text{As}][\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3]$, and $[(\text{CH}_3)_4\text{N}]_2[\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3]$, which form the subject matter for the remainder of this thesis, therefore constitute an interesting and potentially informative series. Firstly the $\text{M}(\text{S}_2\text{C}_6\text{H}_4)_3^{n-}$, ($n = 0, 1, 2$ for $\text{M} = \text{Mo}, \text{Nb}, \text{Zr}$, respectively), moieties form an isoelectronic series so that the only differences are in the central metal. From a molecular orbital viewpoint, this means only the d orbital energies vary throughout the series. Hence, the effect that varying the central metal, and thus the metal d orbitals, will have on the coordination of the metals can be observed, and hopefully correlated to Gray's molecular orbital description for trigonal prismatic geometry. Also since identical ligands ($\text{S}_2\text{C}_6\text{H}_4^{2-}$) are involved, subtle geometry changes involving angles and bond lengths can be more readily compared, than if differing ligands are used.

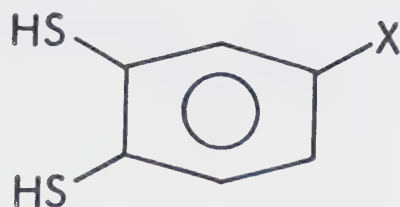
From a comparison of their electronic spectra^{137,143} in Table 18 it is obvious that gross differences exist within the three compounds. For the molybdenum^{137,144} and niobium¹⁴³ complexes the spectra were similar, both having absorptions which were believed characteristic of trigonal prismatic

coordination.¹³⁷ The spectrum¹⁴³ of $\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3^{2-}$ however, was found to be vastly different and was not indicative of a trigonal prism. Thus on the basis of the electronic spectral results it seems that varying the central metal from Mo to Nb to Zr causes changes in the coordination, presumably destabilizing the trigonal prism and favouring a tendency towards octahedral coordination as was observed in $\text{Mo}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$ and $\text{V}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$. It was believed that a complete structural determination of this series of *tris* 1,2-dithiolene complexes would prove useful in understanding further the factors which stabilize trigonal prismatic coordination. It was also of interest to discover whether the electronic spectra were reliable indicators of the coordination geometry in these compounds.

The common 1,2-dithiol ligands and their normal abbreviations, which will be used in this thesis, are shown below.



- X = H dithioglyoxal
 = CN maleonitrile-
 dithiol (mnt)
 = C_6H_5 *cis* 1,2-diphenyl-
 ethene-1,2-dithiol
 (sdt)



X = H benzene-1,2-dithiol
(bdt)

= CH₃ toluene-3,4-dithiol
(tdt)

TABLE 18: ELECTRONIC SPECTRA FOR MOLYBDENUM,
NIOBIUM, AND ZIRCONIUM BENZENE DITHIOLS^{137,143}

COMPLEX	COLOUR	BAND MAXIMA, cm ⁻¹ (ε in parentheses)
Mo(S ₂ C ₆ H ₄) ₃ ¹⁴⁴	Dark Green	11,500 sh (1000); 14,463 (20,900); 22,990 (17,400).
[(C ₆ H ₅) ₄ As][Nb(S ₂ C ₆ H ₄) ₃]	Dark Purple	17,700 (10,700); 27,200 (13,800); 30,700 sh (9,120).
[(C ₂ H ₅) ₄ N] ₂ [Zr(S ₂ C ₆ H ₄) ₃]	Red	20,000 sh (2,030); 35,800 sh (25,200).

CHAPTER VI: THE CRYSTAL AND MOLECULAR STRUCTURE

OF *TRIS* (BENZENE-1,2-DITHIOLATO)

MOLYBDENUM, $[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3]$.

EXPERIMENTAL

Dark green crystals of $\text{Mo}(\text{bdt})_3$ suitable for X-ray diffraction study, prepared by the reaction of molybdenum pentachloride with benzene dithiol,¹³⁷ were kindly supplied by Dr. Takats and Mr. Martin.¹⁴³ Preliminary photography revealed mmm Laué symmetry, indicating an orthorhombic space group. The systematic absences as determined from Weissenberg ($0k\ell$, $1k\ell$; CuK_α X-radiation) and Precession ($h0\ell$, $h1\ell$, $hk0$, hkl ; MoK_α X-radiation) photographs are $0k\ell: k + \ell = 2n + 1$ and $h0\ell: h = 2n + 1$, consistent with the space groups Pnam and $\text{Pna}2_1$. Precise lattice parameters were obtained at 22°C from a least squares refinement of the setting angles of 12 reflections which were accurately centred on a Picker automatic four-circle diffractometer, using CuK_{α_1} X-radiation ($\lambda = 1.54051 \text{ \AA}$). The cell parameters and their standard deviations are: $a = 16.093(3) \text{ \AA}$, $b = 10.177(1) \text{ \AA}$, and $c = 11.906(2) \text{ \AA}$.

The observed density, obtained by floatation in aqueous zinc bromide solution, is $1.74(2) \text{ g cm}^{-3}$ and

is in good agreement with the calculated value of 1.75 g cm^{-3} , obtained assuming four molecules of molecular weight 516.60 a.m.u. per unit cell of volume 1952.84 \AA^3 . For space group $\text{Pna}2_1$ there are 4 general equivalent positions and no restrictions are possible. However for Pnam there are 8 general equivalent positions so the molecules are restricted to lie either on the mirror planes or inversion centres. The *tris* chelate structure cannot have an inversion centre, hence for space group Pnam , the molecule must possess symmetry m .

Intensity data were collected on the Picker automatic four circle diffractometer using CuK_α X-radiation, filtered with 0.0005" thick nickel foil (in preference to a graphite monochromator¹⁴⁵) and using a 2° take-off angle. The crystal was aligned in a general orientation but with its a^* axis approximately coincident with the diffractometer ϕ axis. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as: $\{1,0,0\}$, 0.206 mm; $\{0,1,0\}$, 0.055 mm; $\{0,0,1\}$, 0.077 mm. A coupled $2\theta/\omega$ scan was used, with a 2θ scan speed, of $1^\circ/\text{min}$ to collect all reflections with $2\theta \leq 125^\circ$. The peak scan was approximately two minutes (2°), increasing as the $\alpha_1\alpha_2$ resolution

increased. Stationary background counts of 40 secs. were collected on either side of the peak. Assuming approximate linearity of background, the intensities and standard deviations were calculated as shown previously in Chapter II. The detector was a scintillation counter and was used in conjunction with a pulse height analyzer tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. In addition data collection was interrupted periodically to collect a further five standard reflections to investigate possible decomposition. No significant decomposition was observed over the duration of the data collection. Of the 1806 reflections collected, 1050 were significantly above background with $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects. Terms used in the Zachariasen extinction correction were calculated at this stage. Standard deviations, $\sigma(F)$, in the structure factors were again computed using a "p factor"⁷⁰ of 0.03.

The linear absorption coefficient⁸⁶ using CuK_α radiation is 110.67 cm^{-1} , giving rise to a range of transmission factors between 0.5768 and 0.3099.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened 3-dimensional Patterson map¹⁴⁶ was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 0.5$. The Mo-Mo vectors for both $\text{Pna}2_1$ and Pnam (with the molybdenum atom on the crystallographic mirror) are shown in Table 19. It is obvious that the two space groups cannot be distinguished in the Patterson on the basis of the Mo-Mo vectors alone. However the molybdenum position was obtained as follows. The most intense peak was situated at $(0.500, 0.0, 0.0)$ and was attributed to the vector $(1/2, 1/2-2y, 0)$; thus the y coordinate was obtained as ± 0.25 . The accidentally special y coordinate leads to an ambiguity in the assignment of the next most intense peaks, observed at $(0.325, 0.500, 0.500)$ and $(0.182, 0.500, 0.500)$, as vectors of the form $(1/2-2x, 1/2, 1/2)$ and $(2x, 2y, 1/2)$. Because of this failure to identify the true Harker line vector, two possible solutions for molybdenum coordinates had to be tested by subsequent structure factor calculations and least squares refinement. The solutions to be tested were (a) $x = 0.09$, $y = 0.25$, $z = 0.25$, and (b) $x = 0.16$, $y = 0.25$ and $z = 0.25$.

The fourth largest peak on the map, at $(0.0, 0.0,$

TABLE 19: HARKER VECTORS FOR $\text{Mo}(\text{bdt})_3$

$\text{Pna}2_1$		$\text{Pnam} (z=1/4), \text{ SPECIAL POSITION "C"}$	
VECTOR FORM	WEIGHT	VECTOR FORM	WEIGHT
$1/2-2x, 1/2, 1/2$	2	$1/2-2x, 1/2, 1/2$	2
$1/2+2x, 1/2, 1/2$	2	$1/2+2x, 1/2, 1/2$	2
$1/2, 1/2-2y, 0$	2	$1/2, 1/2-2y, 0$	2
$1/2, 1/2+2y, 0$	2	$1/2, 1/2+2y, 0$	2
$2x, 2y, 1/2$	1	$2x, 2y, 1/2$	1
$-2x, -2y, 1/2$	1	$-2x, -2y, 1/2$	1
$2x, -2y, 1/2$	1	$2x, -2y, 1/2$	1
$-2x, 2y, 1/2$	1	$-2x, 2y, 1/2$	1

0.255), was located at 3.04 \AA from the origin and was consistent with a build-up of S-S vectors between sulfur atoms related by a mirror perpendicular to z . Since this was the largest S-S vector, the possibility of the mirror bisecting the triangular faces was excluded and the space group was probably Pnam with the mirror relating the two triangular faces of the trigonal prism. If this were the case, then Mo-S vectors should be observed at w coordinates of about $1/2(0.255) \approx 0.13$. Three vectors at $2.3 - 2.4 \text{ \AA}$ from the origin were located with w coordinates 0.136 and were consistent with the trigonal prismatic geometry. In addition three vectors were located in the $w = 0$ plane at $3.04 - 3.17 \text{ \AA}$ from the origin and these were consistent with vectors between the sulfur atoms within the triangular faces. From the Mo-S and S-S vectors the sulfur positions were calculated as either: S1(0.11, 0.14, 0.38), S2(0.16, 0.42, 0.38) and S3(0.29, 0.21, 0.38) corresponding to Mo position (b) or S1(0.04, 0.14, 0.38), S2(0.09, 0.42, 0.38) and S3(0.22, 0.21, 0.38) corresponding to Mo position (a).

To obtain the proper x coordinates a least squares refinement was performed with the model based on Mo positions (b). This model showed no signs of successful

refinement and converged after two cycles to give $R_1 = 0.424$ and $R_2 = 0.516$. However the model based on Mo coordinates (a) refined to $R_1 = 0.349$ and $R_2 = 0.435$ in two cycles. Temperature factors were fixed in these cycles, so further refinement of the second model, varying the temperature factors yielded $R_1 = 0.209$ and $R_2 = 0.294$ after the three cycles and thus the model was assumed to be correct. An outline of the solution and refinement is shown in Table 20.

TABLE 20: REFINEMENT OUTLINE

	Model	R_1	R_2
(1)	Mo and S atoms based on Mo coordinates (0.16,0.25,0.25)	0.424	0.516
(2)	Mo and S atoms based on Mo coordinates (0.09,0.25,0.25)	0.349	0.435
(3)	Mo and S atoms of model (2) - varying temperature factors	0.209	0.294
(4)	Mo, S, and C atoms; isotropic B's	0.079	0.086
(5)	Absorption Correction	0.065	0.075
(6)	Mo and S atoms anisotropic	0.050	0.062
(7)	H positions added	0.046	0.051
(8)	Extinction correction ¹⁴⁷	0.042	0.042
(9)	Carbon atoms anisotropic	0.035	0.034

Structure factors were calculated using the atomic scattering factors of the neutral atoms for molybdenum,

sulfur and carbon compiled by Cromer and Mann.⁷⁵ The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.¹⁴⁹ In addition anomalous dispersion corrections,⁷⁶ both real and imaginary, were applied to the molybdenum and sulfur scattering factors ($\Delta f'_{\text{Mo}} = -0.54$, $\Delta f''_{\text{Mo}} = 2.89$, $\Delta f'_S = 0.31$, $\Delta f''_S = 0.58$).

The carbon atoms were located from an electron density difference map phased on model (3). Anisotropic temperature factors for the different groups of atoms were introduced, as indicated by features in electron density difference maps, and can be justified, at the 0.005 significance level, by the subsequent application of Hamilton's R factor ratio test.⁷⁹ In the difference map, phased on model (6), the hydrogen atoms were visible so they were included in subsequent refinements, their positions calculated from the known geometry and orientation of the benzene rings, and using a C-H distance of 1.0 Å. The hydrogen atoms were assigned thermal parameters approximately 15% higher than those of the attached carbon atoms. Although they were included in the structure factor calculations, their parameters were not refined.

Extinction corrections¹⁴⁷ were applied since comparison of $|F_o|$ and $|F_c|$ for low angle reflections suggested the problem may exist. Verification of the

importance of the extinction correction is evident in the results of the refinements before and after this correction. Before the correction, all reflections except one with $\sin \theta/\lambda \leq 0.084$ were rejected from the refinement on the basis that $|\Delta F/\sigma(F)| > 5.0$, and in all cases $|F_o|$ was less than $|F_c|$ for these reflections. After the extinction correction, only one of these reflections previously rejected was still rejected from the refinement. The final refined value of the extinction scale factor, C , is 2.371×10^{-6} .

Anomalous features in the thermal parameters (*vide infra*) suggested that the scattering factors could be inadequate. Several refinements were attempted using various alternative scattering factors [Mo(IV),¹⁵⁰ Mo(VI),¹⁵⁰ S⁻⁷⁵] but no better agreement in R factor and no more reasonable thermal parameters were obtained. Thus the results from the original refinement are reported.

Programmes used in solution, refinement and presentation of data are listed in Appendix 2.

RESULTS

The observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 21. The final fractional coordinates of all atoms and their isotropic temperature factors are shown in Table 22, their standard deviations being obtained from the inverse matrix of the final least squares analysis. The anisotropic thermal parameters⁸⁰ (U_{ij} 's) of all anisotropic atoms are shown in Table 23. Relevant intramolecular bond lengths are shown in Table 24 and the intramolecular angles in Table 25. Intermolecular contacts which are close to the predicted van der Waals separations¹⁵¹ are listed in Table 26. These bond lengths, intermolecular contacts and bond angles, along with their standard deviations were obtained from ORFFE (See Appendix 2). Several least squares plane calculations are shown in Table 27, along with the deviations of the atoms from the planes. In addition, Table 28 shows the dihedral angles between selected planes.

In the three dimensional drawings of the molecule, 50% probability thermal ellipsoids are shown for molybdenum and sulfur atoms. For the carbon atoms artificially low isotropic thermal parameters were used

for clarity of the diagram. Similarly the hydrogen atoms were excluded from the plot for clarity. The hydrogen atoms are numbered from H1 to H6 and are bonded sequentially to the second and third carbon atoms in the rings. In the packing diagram in Fig. 13, the open bonds represent molecules at $z = 0.25$ whereas the dark bonds represent molecules at $z = 0.75$.

TABLE 21: OBSERVED AND CALCULATED STRUCTURE
FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 0**																			
0	2	3512	3133	2	5	455	442	0	5	579	582	6	2	338	294	6	1	578	579
0	4	2258	2159	2	6	148	108	0	5	646	663	6	3	331	332	6	2	245	335
0	6	628	664	2	11	240	241	0	7	1625	1585	6	5	488	454	6	3	804	776
0	8	2010	1969	3	0	856	850	0	8	815	803	6	6	350	339	6	5	505	483
0	12	404	428	3	1	642	635	0	9	896	868	6	7	825	809	6	6	285	273
1	1	2346	2421	3	2	136	143	0	13	288	300	6	9	639	630	6	7	617	595
1	3	278	258	3	3	370	383	1	0	1800	1761	6	10	220	201	6	8	472	442
1	5	440	459	3	4	912	911	1	1	604	620	6	11	304	270	6	9	255	268
1	7	2098	2060	3	5	390	395	1	2	961	978	7	0	766	777	6	11	384	393
1	9	1115	1098	3	7	205	157	1	3	373	363	7	1	451	468	7	0	911	914
1	13	245	276	3	8	371	375	1	4	442	440	7	2	720	714	7	1	883	903
2	0	520	515	3	10	257	266	1	5	443	445	7	4	627	619	7	4	852	853
2	2	836	852	3	11	265	286	1	6	1153	1160	7	6	528	490	7	7	532	508
2	4	1147	1168	3	12	375	347	1	7	594	591	7	7	496	472	7	8	565	560
2	6	1371	1333	4	0	577	587	1	8	1205	1190	7	8	385	383	7	9	244	254
2	8	1089	1067	4	1	164	149	1	9	395	379	7	9	312	317	8	0	664	673
2	10	608	604	4	2	472	457	1	10	429	422	7	10	327	338	8	1	363	366
2	12	420	429	4	3	1447	1417	1	12	217	206	8	0	303	323	8	2	294	317
3	1	798	823	4	4	996	996	1	13	161	168	8	3	935	920	8	3	391	414
3	3	1888	1895	4	5	651	671	2	0	435	420	8	5	745	765	8	5	269	281
3	5	1397	1365	4	7	718	708	2	1	2428	2530	8	6	321	322	8	6	266	272
3	7	421	416	4	8	549	541	2	2	775	794	8	8	351	338	8	7	292	299
3	9	474	477	4	9	312	333	2	3	774	800	8	9	174	157	8	8	362	319
3	11	742	740	4	10	190	142	2	4	980	990	9	0	314	323	9	1	209	205
3	13	460	444	4	11	452	413	2	5	494	520	9	1	546	532	9	3	330	339
4	0	666	679	4	12	319	307	2	6	250	226	9	2	585	587	9	5	273	305
4	2	902	900	5	0	230	213	2	7	763	760	9	4	684	681	10	2	224	234
4	4	1148	1168	5	1	281	290	2	9	696	699	9	6	246	233	10	3	171	160
4	6	779	765	5	3	655	652	2	10	421	393	9	7	341	334	10	4	435	428
4	8	640	631	5	4	389	402	2	11	367	380	10	0	640	654	10	6	180	193
4	10	790	793	5	5	400	402	2	12	375	384	10	1	271	279	11	0	263	246
4	12	550	539	5	6	172	131	2	13	247	264	10	2	201	197	11	1	165	132
5	1	974	992	5	7	340	335	3	0	709	698	10	3	397	415	11	3	333	329
5	3	823	835	5	10	238	255	3	1	586	573	10	4	174	190	11	4	162	190
5	5	811	803	5	11	358	331	3	2	1079	1095	10	5	351	378	**H = 4****			
5	7	761	766	5	12	164	169	3	3	1576	1579	10	6	168	191	0	0	672	672
5	9	617	627	6	0	230	242	3	4	1260	1256	10	7	265	268	0	1	2502	2546
5	11	456	435	6	1	551	557	3	5	1119	1113	11	0	357	383	0	2	1074	1093
6	0	1262	1263	6	2	196	235	3	6	788	785	11	1	458	442	0	3	705	719
6	2	1248	1228	6	4	553	535	3	7	374	368	11	2	305	295	0	4	1255	1262
6	4	923	891	6	7	519	484	3	8	470	479	11	4	218	215	0	5	357	372
6	6	568	544	6	9	295	310	3	10	492	496	**H = 3****				0	6	319	311
6	8	331	303	7	0	1080	1110	3	11	634	656	1	1	1486	1493	0	7	630	635
6	10	184	233	7	2	206	193	3	12	431	437	1	3	623	619	0	9	591	610
7	1	902	888	7	3	239	268	3	13	306	296	1	5	532	515	0	10	508	504
7	3	785	786	7	4	525	501	4	0	665	656	1	7	325	320	0	11	266	334
7	5	611	600	7	5	207	195	4	1	882	874	1	9	214	129	0	12	500	515
7	7	440	430	7	6	347	314	4	2	703	686	1	11	301	286	0	13	257	239
7	9	383	388	7	8	687	668	4	3	1181	1175	2	0	1679	1671	1	0	275	242
8	2	411	392	8	1	370	360	4	4	1494	1476	2	1	258	258	1	1	456	459
8	4	749	765	8	4	299	304	4	5	925	922	2	2	628	624	1	2	593	637
8	6	565	585	8	7	408	434	4	6	211	188	2	4	388	401	1	3	1224	1240
8	8	464	457	8	9	172	216	4	7	597	587	2	8	188	225	1	4	1351	1297
8	10	504	515	9	2	275	279	4	8	378	382	3	0	276	275	1	5	1131	1142
9	1	583	583	9	3	282	282	4	9	475	443	3	4	207	171	1	6	653	698
9	3	656	648	9	4	533	525	4	10	347	335	3	5	256	241	1	7	231	235
9	5	461	463	9	5	284	290	4	11	411	422	3	7	201	211	1	8	542	529
9	7	280	267	10	3	588	601	4	12	500	506	4	0	571	555	1	9	242	270
10	0	227	256	10	4	320	300	5	0	1245	1235	4	2	177	174	1	10	556	508
10	2	381	380	10	5	388	397	5	1	341	356	4	4	652	670	1	11	559	582
10	4	485	479	10	7	168	173	5	2	840	827	4	6	245	214	1	12	462	481
10	6	388	391	11	0	164	76	5	3	699	697	4	10	209	200	1	13	255	317
11	1	395	407	11	1	175	177	5	4	487	476	4	12	225	214	2	0	449	443
11	3	263	297	11	2	240	241	5	5	483	487	5	0	711	702	2	2	792	798
H = 1**				11	3	180	193	5	6	741	729	5	4	551	532	2	3	1852	1908
1	0	128	157	11	4	443	457	5	8	613	778	5	7	428	403	2	4	646	937
2	0	581	590	**H = 2****				5	10	436	422	5	8	294	293	2	5	1444	1451
2	1	721	741	0	0	1296	1329	5	11	318	299	5	9	405	426	2	6	520	515
2	3	400	416	0	1	2124	2030	5	12	216	238	5	11	192	180	2	8	270	267
2	4	335	335	0	2	417	434	6	0	535	541	5	12	232	204	2	9	247	210
				0	3	195	185	6	1	859	869	6	0	846	843				

Table 21 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 4**				9	4	237	280	8	8	247	263	6	2	796	783	6	3	459	501
2	10	369	350	9	5	308	327	8	9	207	212	6	3	245	261	6	5	391	395
2	11	777	783	9	6	239	230	9	0	219	242	6	4	201	161	7	0	236	225
2	12	329	340	9	8	228	255	9	2	216	228	6	5	223	196	7	3	193	142
2	13	416	424	10	1	379	420	9	3	185	190	6	6	580	573	7	4	398	396
3	1	1205	1190	10	2	229	257	9	5	236	248	6	8	701	666	7	6	190	186
3	2	1503	1472	10	4	380	395	9	6	197	223	6	10	195	214	8	3	336	322
3	3	614	606	10	5	175	193	10	1	412	422	7	0	284	267	8	5	280	293
3	4	2093	2040	10	6	177	176	10	4	350	315	7	1	805	803	8	8	197	186
3	5	399	383	11	0	569	571	11	0	427	440	7	3	589	585	9	1	286	305
3	6	298	291	11	1	224	258	11	2	242	232	7	5	526	500	9	2	194	234
3	7	462	475	11	2	159	177	**H = 6****				7	7	450	442	9	4	360	331
3	8	391	395	11	3	179	187	0	0	1346	1359	7	9	324	314	9	7	220	249
3	9	356	331	**H = 5****				0	1	542	554	8	0	219	167	10	0	327	337
3	10	519	486	1	0	1106	1070	0	2	1742	1693	8	1	236	231	10	3	247	237
3	12	673	682	1	1	670	673	0	3	1265	1274	8	2	401	409	**H = 8****			
4	0	1485	1455	1	2	125	132	0	4	1566	1540	8	4	902	910	0	0	1116	1124
4	1	590	594	1	3	176	214	0	5	738	753	8	6	496	483	0	1	1307	1282
4	2	616	605	1	4	624	620	0	6	531	533	8	7	293	270	0	2	297	293
4	3	990	1000	1	5	228	223	0	7	645	659	9	0	356	348	0	3	798	815
4	5	781	783	1	6	206	182	0	9	257	263	9	1	260	257	0	4	334	331
4	6	480	488	1	7	169	208	0	10	479	470	9	3	636	640	0	5	634	621
4	7	306	298	1	8	435	436	0	11	498	506	9	4	205	180	0	6	246	261
4	8	719	734	1	11	210	189	0	12	541	564	9	5	508	521	0	7	603	604
4	9	446	451	1	12	196	223	1	0	949	914	10	0	308	305	0	8	479	475
4	10	234	232	2	1	581	602	1	1	474	476	10	2	324	339	0	9	566	568
4	11	558	568	2	2	285	293	1	2	245	265	10	4	359	358	0	11	418	422
5	0	723	730	2	3	971	970	1	3	1719	1733	11	1	513	523	1	1	450	440
5	1	528	921	2	4	295	291	1	4	1059	1057	**H = 7****				1	2	688	695
5	2	424	441	2	5	381	384	1	5	1302	1316	1	0	1099	1049	1	3	148	62
5	4	329	353	2	6	273	253	1	7	330	299	1	2	252	248	1	4	873	879
5	5	265	236	2	7	566	951	1	8	408	427	1	3	310	282	1	6	808	815
5	6	756	756	2	8	309	349	1	9	361	346	1	4	999	978	1	7	449	451
5	7	742	733	2	9	433	449	1	10	251	226	1	6	212	194	1	8	638	651
5	8	824	807	2	11	322	353	1	11	707	693	1	7	210	230	1	9	278	252
5	9	413	440	3	0	1563	1561	1	12	352	362	1	8	689	698	1	10	501	494
5	10	409	414	3	4	1085	1074	2	0	683	677	1	12	257	264	1	12	353	363
5	12	175	200	3	6	291	307	2	2	1009	1042	2	0	354	339	2	1	1130	1137
6	0	575	577	3	8	878	874	2	3	318	328	2	1	678	677	2	3	773	776
6	1	915	937	3	12	312	302	2	4	1231	1296	2	3	477	474	2	4	196	203
6	2	465	444	4	0	237	217	2	5	275	252	2	5	280	262	2	5	625	634
6	3	386	395	4	1	1109	1074	2	6	651	647	2	7	520	535	2	6	268	268
6	4	351	321	4	2	315	292	2	8	434	431	2	8	250	240	2	7	644	650
6	5	400	411	4	3	206	170	2	10	719	746	2	9	221	216	2	8	224	240
6	6	431	449	4	4	550	555	2	12	554	568	2	11	274	261	2	9	531	523
6	7	665	675	4	7	200	175	3	0	173	192	3	1	262	293	2	11	332	328
6	8	421	402	4	8	317	324	3	1	342	346	3	3	296	310	3	0	1256	1240
6	9	352	360	4	12	163	166	3	3	1034	1072	3	4	167	140	3	1	430	418
7	0	888	881	5	0	206	173	3	5	1054	1060	3	7	400	415	3	2	986	980
7	1	330	313	5	3	185	189	3	6	229	220	4	0	805	791	2	3	267	249
7	2	563	565	5	5	177	176	3	7	644	654	4	1	295	302	3	4	620	604
7	3	386	396	5	6	244	258	3	8	243	240	4	2	180	191	3	5	181	138
7	4	288	295	5	8	241	288	3	9	604	613	4	3	707	714	3	6	579	559
7	5	398	391	5	11	165	98	3	11	572	589	4	4	323	329	3	8	535	534
7	6	483	466	6	0	526	544	4	0	941	953	4	5	466	464	3	10	321	343
7	7	325	300	6	1	213	190	4	1	227	220	4	6	209	159	4	0	883	883
7	8	453	459	6	4	238	222	4	2	797	795	4	7	357	335	4	1	990	973
7	9	277	274	6	5	213	237	4	4	625	631	4	8	335	345	4	2	229	254
7	10	220	223	6	7	226	274	4	6	605	793	4	11	262	261	4	3	505	489
8	1	358	340	6	8	295	253	4	8	781	773	5	0	295	276	4	4	309	286
8	2	254	265	7	0	605	602	4	10	442	440	5	1	603	585	4	5	463	458
8	3	395	435	7	1	670	664	4	12	227	270	5	2	218	236	4	6	217	188
8	4	563	554	7	2	261	274	5	1	1480	1458	5	3	301	262	4	7	722	695
8	5	484	456	7	3	282	290	5	2	218	175	5	4	605	605	4	8	428	443
8	6	311	295	7	5	247	248	5	3	308	273	5	5	188	153	4	9	540	567
8	7	380	375	7	7	351	341	5	4	317	318	5	7	345	375	4	11	296	273
8	9	295	303	7	8	322	300	5	5	330	296	5	8	242	240	5	0	818	815
9	0	710	722	8	0	200	210	5	7	588	940	5	9	190	205	5	1	721	728
9	1	291	295	8	1	241	257	5	9	601	608	5	10	236	257	5	2	602	596
9	2	532	538	8	6	189	204	5	10	177	87	6	0	385	386	5	3	422	411
9	3	496	515	8	7	291	288	6	0	1456	1486	6	2	239	232				

TABLE 22: ATOM COORDINATES AND
ISOTROPIC TEMPERATURE FACTORS

ATOM	x	y	z	B
Mo	0.08815(5)	0.25886(7)	0.25	2.46*
S1	0.0077(1)	0.1371(1)	0.3802(1)	3.28*
S2	0.0632(1)	0.4286(1)	0.3808(1)	3.48*
S3	0.1939(1)	0.2047(1)	0.3808(1)	3.36*
C1	-0.0757(4)	0.0681(5)	0.3096(5)	3.19*
C2	-0.1390(5)	0.0016(7)	0.3648(7)	4.51*
C3	-0.1989(4)	-0.0638(7)	0.3087(7)	4.94*
C4	0.0787(4)	0.5741(5)	0.3091(5)	3.32*
C5	0.0872(5)	0.6936(6)	0.3659(6)	4.55*
C6	0.0959(5)	0.8080(6)	0.3088(7)	6.00*
C7	0.2557(4)	0.0951(6)	0.3091(5)	3.26*
C8	0.3073(4)	0.0067(7)	0.3677(7)	4.30*
C9	0.3565(4)	-0.0801(7)	0.3096(7)	5.30*
H1	-0.1389	0.0016	0.4488	5.2
H2	-0.2438	-0.1121	0.3518	6.0
H3	0.0873	0.6937	0.4499	5.2
H4	0.1023	0.8921	0.3514	6.0
H5	0.3074	0.0066	0.4516	5.2
H6	0.3925	-0.1429	0.3523	6.0

* These values are equivalent isotropic temperature factors⁸¹ corresponding to the anisotropic thermal parameters shown in Table 23.

TABLE 23: ANISOTROPIC TEMPERATURE FACTORS (\AA^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.0389(4)	0.0259(3)	0.0287(3)	-0.0003(4)	0.0	0.0
S1	0.0489(10)	0.0400(8)	0.0356(8)	-0.0053(8)	-0.0006(9)	0.0033(8)
S2	0.0547(11)	0.0364(8)	0.0409(9)	0.0026(8)	0.0030(9)	-0.0070(8)
S3	0.0455(10)	0.0461(9)	0.0358(8)	0.0015(8)	-0.0049(8)	-0.0027(7)
Cl	0.039(4)	0.034(3)	0.048(4)	0.002(3)	0.000(3)	-0.001(3)
C2	0.051(5)	0.064(5)	0.056(5)	-0.006(4)	0.014(4)	0.016(4)
C3	0.039(4)	0.074(5)	0.075(6)	-0.019(4)	0.012(4)	0.008(4)
C4	0.034(4)	0.033(3)	0.059(4)	0.004(3)	-0.002(3)	-0.007(3)
C5	0.057(5)	0.040(3)	0.075(5)	0.015(4)	0.004(5)	-0.013(4)
C6	0.079(6)	0.037(4)	0.111(7)	0.011(4)	0.005(5)	-0.010(4)
C7	0.034(4)	0.044(4)	0.046(4)	-0.000(3)	-0.002(3)	-0.004(3)
C8	0.048(5)	0.061(4)	0.054(5)	0.005(4)	-0.001(4)	0.004(4)
C9	0.045(5)	0.068(5)	0.088(7)	0.011(4)	-0.009(4)	0.014(4)

TABLE 24: INTRAMOLECULAR CONTACTS ($\overset{\circ}{\text{\AA}}$)

ATOMS	DISTANCE ($\overset{\circ}{\text{\AA}}$)	ATOMS	DISTANCE ($\overset{\circ}{\text{\AA}}$)
Mo-S1	2.370(2)	Mo-S2	2.360(2)
Mo-S3	2.371(2)	S1-S1'	3.100(3)
S2-S2' ^a	3.115(3)	S3-S3'	3.114(3)
S1-S2	3.099(2)	S1-S3	3.074(2)
S2-S3	3.101(2)	S1-C1	1.731(6)
S2-C4	1.728(6)	S3-C7	1.721(6)
C1-C1'	1.419(11)	C1-C2	1.388(8)
C2-C3	1.349(10)	C3-C3'	1.394(16)
C4-C4'	1.408(12)	C4-C5	1.398(8)
C5-C6	1.355(8)	C6-C6'	1.400(16)
C7-C7'	1.408(12)	C7-C8	1.410(8)
C8-C9	1.373(10)	C9-C9'	1.418(16)

^aPrimed atoms are related by a mirror at $z = 1/4$.

TABLE 25: INTRAMOLECULAR ANGLES (DEGREES)

ATOMS	ANGLES	ATOMS	ANGLES
S1-Mo-S1' ^a	81.70 (8)	S2-Mo-S2'	82.57 (8)
S3-Mo-S3'	82.09 (8)	S1-Mo-S2	81.85 (5)
S1-Mo-S3	80.85 (6)	S2-Mo-S3	81.89 (6)
S1-Mo-S2'	136.17 (7)	S1-Mo-S3'	134.43 (6)
S2-Mo-S3'	136.51 (7)	Mo-S1-C1	108.5 (2)
Mo-S2-C4	106.1 (2)	Mo-S3-C7	103.9 (2)
S1-C1-C1'	119.0 (2)	S2-C4-C4'	119.6 (2)
S3-C7-C7'	119.7 (2)	C2-C1-C1'	118.2 (4)
C1-C2-C3	122.1 (8)	C2-C3-C3'	119.7 (5)
C5-C4-C4'	118.9 (4)	C4-C5-C6	120.9 (7)
C5-C6-C6'	120.1 (4)	C8-C7-C7'	119.7 (4)
C7-C8-C9	120.0 (7)	C8-C9-C9'	120.3 (5)
S3-S1-S2	60.30 (5)	S1-S3-S2	60.24 (5)
S1-S2-S3	59.46 (5)		

^aPrimed atoms are related by a mirror at $z = 1/4$.

TABLE 26: INTERMOLECULAR CONTACTS (\AA)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
S1	H4	$x, y-1, z$	2.941
S1	H3	$\bar{x}, \bar{y}+1, \bar{z}+1$	3.065
S2	H5	$1/2-x, 1/2+y, \bar{z}+1$	2.992
S3	H1	$\bar{x}, \bar{y}, \bar{z}+1$	3.051
S1	C6	$x, y-1, z$	3.736 (7)
S1	C5	$\bar{x}, \bar{y}+1, \bar{z}+1$	3.800 (7)
S2	C8	$1/2-x, 1/2+y, \bar{z}+1$	3.734 (8)
S2	C9	$1/2+x-1, 1/2-y, z$	3.763 (7)
S3	C2	$\bar{x}, \bar{y}, \bar{z}+1$	3.791 (7)
S2	S2	$\bar{x}, \bar{y}+1, \bar{z}+1$	3.782 (3)
C3	C4	$1/2+x-1, 1/2-y, z$	3.581 (9)
C3	C9	$1/2+x-1, 1/2-y-1, z$	3.733 (10)
C3	C5	$1/2+x-1, 1/2-y, z$	3.749 (10)
C4	C9	$1/2+x-1, 1/2-y, z$	3.577 (9)
C4	C3	$1/2+x, 1/2-y, z$	3.581 (9)
C4	H6	$1/2+x-1, 1/2-y, z$	3.120
C5	H6	$1/2+x-1, 1/2-y, z$	3.180
C4	H2	$1/2+x, 1/2-y, z$	2.927
C5	H2	$1/2+x, 1/2-y, z$	2.848

TABLE 27: LEAST SQUARES PLANE CALCULATIONS^a

(A)	ATOMS DEFINING PLANE: S1, Mo, S1'			
	EQUATION OF PLANE: $-0.6913X + 0.7225Y - 0.9227 = 0.0$			
(B)	ATOMS DEFINING PLANE: S2, Mo, S2'			
	EQUATION OF PLANE: $-0.9740X - 0.2266Y + 1.9797 = 0.0$			
(C)	ATOMS DEFINING PLANE: S3, Mo, S3'			
	EQUATION OF PLANE: $-0.3080X - 0.9514Y + 2.9444 = 0.0$			
(D)	ATOMS DEFINING PLANE: S1, S2, S3			
	EQUATION OF PLANE: $-0.0016X - 0.0019Y + 1.0Z - 4.5264 = 0.0$			
	DISTANCE OF Mo FROM PLANE (\AA): -1.556			
(E)	ATOMS DEFINING PLANE: S1', S2', S3'			
	EQUATION OF PLANE: $0.0016X - 0.0019Y + 1.0Z - 1.4298 = 0.0$			
	DISTANCE OF Mo FROM PLANE (\AA): 1.556			
(F)	ATOMS DEFINING PLANE: S1, S1', C1, C1', C2, C2', C3, C3'			
	EQUATION OF PLANE: $0.5094X - 0.8605Y + 1.1429 = 0.0$			
	DISTANCES OF ATOMS FROM PLANE (\AA):			
	S1	0.005(2)	S1'	0.005(2)
	C1	-0.074(6)	C1'	-0.074(6)
	C2	-0.011(7)	C2'	-0.011(7)
	C3	0.071(8)	C3'	0.071(8)
	Mo	-0.4017(7)		

TABLE 26 (Continued)

(G) ATOMS DEFINING PLANE: S2, S2', C4, C4', C5, C5',
C6, C6'

EQUATION OF PLANE: $-0.9899X + 0.1420Y + 0.3898 = 0.0$

DISTANCES OF ATOMS FROM PLANE ($\overset{\circ}{\text{\AA}}$):

S2	0.002(2)	S2'	0.002(2)
C4	-0.035(6)	C4'	-0.035(6)
C5	0.001(7)	C5'	0.001(7)
C6	0.028(8)	C6'	0.028(8)
Mo	-0.6412(7)		

(H) ATOMS DEFINING PLANE: S3, S3', C7, C7', C8, C8',
C9, C9'

EQUATION OF PLANE: $0.7424X + 0.6700Y - 3.7136 = 0.0$

DISTANCES OF ATOMS FROM PLANE ($\overset{\circ}{\text{\AA}}$):

S3	0.000(2)	S3'	0.000(2)
C7	-0.008(6)	C7'	-0.008(6)
C8	0.006(7)	C8'	0.006(7)
C9	0.001(7)	C9'	0.001(7)
Mo	-0.8942(7)		

aX , Y, and Z are in $\overset{\circ}{\text{\AA}}$ and refer to the orthogonal
coordinates along a , b , and c^* .

TABLE 28: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE
S1,Mo,S1'	S2,Mo,S2'	120.7°
S1,Mo,S1'	S3,Mo,S3'	118.2°
S2,Mo,S2'	S3,Mo,S3'	121.1°
S1,Mo,S1'	S1,S1',C1,C1',C2,C2',C3,C3'	13.1°
S2,Mo,S2'	S2,S2',C4,C4',C5,C5',C6,C6'	21.1°
S3,Mo,S3'	S3,S3',C7,C7',C8,C8',C9,C9'	30.0°

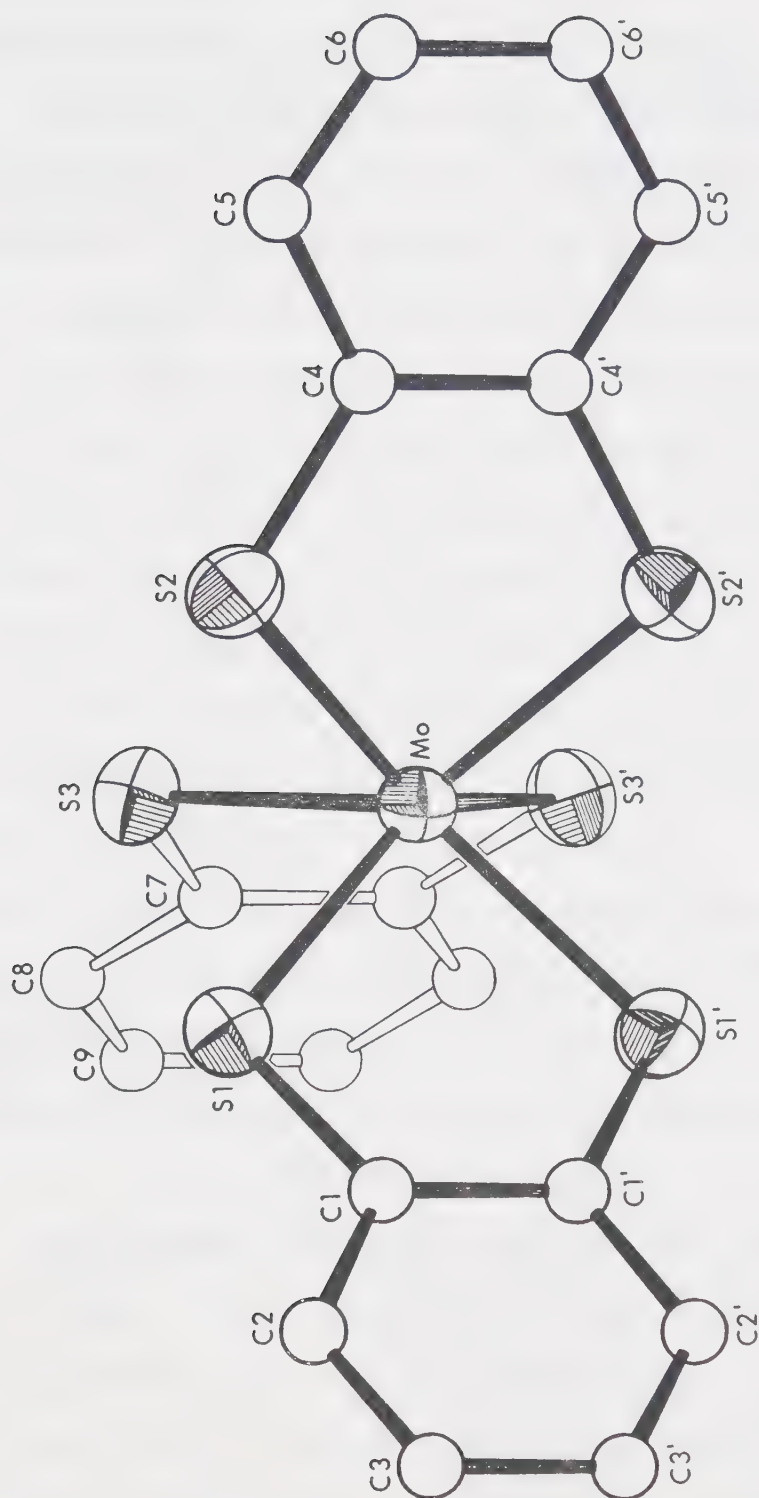


Fig. 9: A PERSPECTIVE VIEW OF $\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$.

DESCRIPTION OF STRUCTURE

A 3-dimensional view of $\text{Mo}(\text{bdt})_3$ is shown in Fig. 9. The sulfur atoms surround the molybdenum in an almost perfect trigonal prismatic coordination with the dithiolene ligands radiating from the molybdenum atom in a "paddle-wheel" arrangement. The molecule deviates from approximate D_{3h} symmetry due to the bending of the $(\text{S}_2\text{C}_6\text{H}_4)$ planes from the MoS_2 planes by an average of 21.4° . In addition C_{3h} symmetry is not achieved due to the three differing $(\text{S}_2\text{C}_6\text{H}_4)/\text{MoS}_2$ dihedral angles (Fig. 12). The molybdenum atom is located on the crystallographic mirror at $z = 1/4$, with the two triangular faces of the prism being related by the mirror.

Again, as was the case for the three previous trigonal prismatic structures, $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$,¹²⁹ $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ ¹³⁰ and $\text{V}(\text{S}_2\text{C}_2\text{Ph}_2)_3$,¹³² the intra- and interligand sulfur-sulfur distances are approximately equal (3.110 \AA and 3.091 \AA respectively in the present study). These agree favourably with those observed in other prisms and are especially close to those in $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ (Table 48). It is interesting that the relative magnitudes of these intra- and interligand S-S distances are reversed to those in the other three

dithiolene trigonal prisms, with the intraligand S-S distances being greater in the present study. This can be attributed to the constraint of the fixed ligand bite holding the intraligand sulfurs apart. That the ligand bite should be greater in the benzene dithiols than in the ethylene dithiols is apparent since the C-C distances in the former are longer, thereby ensuring a larger bite. This was also observed in the trigonal prismatic molecule¹⁵² $\text{Mo}[\text{Se}_2\text{C}_2(\text{CF}_3)_2]_3$, which also has intraligand Se-Se distances which exceed the interligand values [$3.317(5) \text{ \AA}$ and $3.222(3) \text{ \AA}$ respectively].

The mean Mo-S distance (2.367 \AA), although similar to the metal-sulfur distance in other trigonal prisms, is significantly longer than their average of approximately 2.33 \AA . In fact they are more closely matched by the metal-sulfur distances in the non-trigonal prismatic species $\text{V}(\text{mnt})_3^{2-}$ ¹⁴⁰ and $\text{Mo}(\text{mnt})_3^{2-}$ ¹⁴¹ (Table 48). This difference is again probably due to the difference in ligands, all previous examples being substituted ethylene dithiol ligands. For this reason a rigid comparison of intramolecular distances and angles will prove more worthwhile within the series of compounds which are the topic of part of this thesis, i.e., $\text{Mo}(\text{bdt})_3$, $[\text{Ph}_4\text{As}][\text{Nb}(\text{bdt})_3]$, and $[(\text{CH}_3)_4\text{N}]_2[\text{Zr}(\text{bdt})_3]$. In addition the molybdenum-

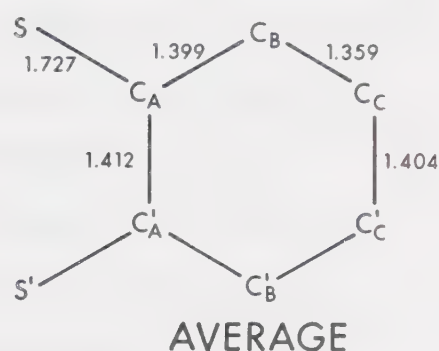
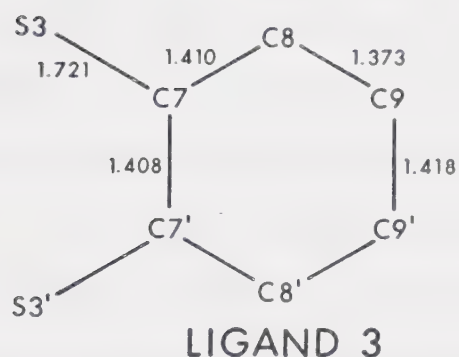
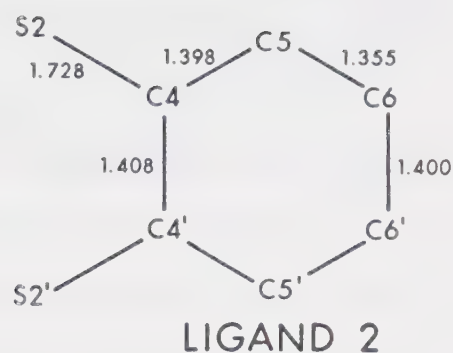
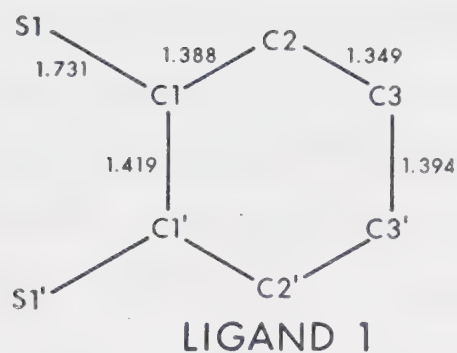


Fig. 10: DIMENSIONS WITHIN THE DITHIOLENE LIGANDS.

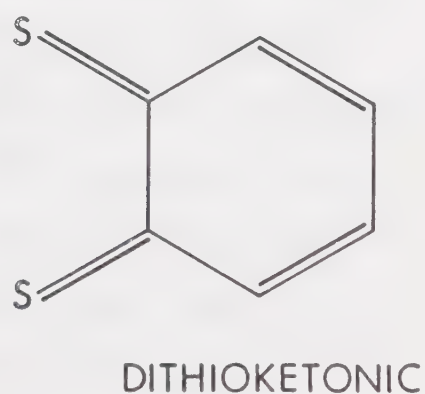
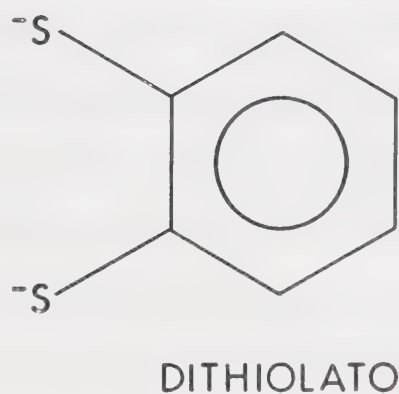


Fig. 11: DITHIOLATO AND DITHIOKETONIC LIMITING FORMULATIONS FOR THE "bdt" LIGAND.

sulfur distances are again shorter than those observed in the 1,1-dithiolato complexes, $\text{Fe}[\text{S}_2\text{CN}(\text{n-C}_4\text{H}_9)_2]_3$,¹⁵³ $\text{Ru}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$,¹⁵⁴ $\text{Cr}[\text{S}_2\text{P}(\text{CH}_3)_2]_3$,¹⁵⁵ and $\text{V}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3$,¹⁵⁶ although the molybdenum covalent radius is greater than any of these metal radii.¹³³ Thus a difference in the metal-sulfur bonding between the 1,1-dithiolato and 1,2-dithiolene complexes is obvious with the latter having a greater amount of M-S bonding. This is in agreement with the proposed metal-sulfur multiple bonding in the *tris*(1,2-dithiolenes).¹⁵⁷

The sulfur-carbon distances (mean 1.727 Å) are similar to those in the other trigonal prisms and are once again consistent with a great deal of S=C double bond character, as witnessed by their similarity with the double bonded S=C distance of 1.72 Å in thiourea¹³⁴ $[\text{SC}(\text{NH}_2)_2]$ and its derivatives.¹³⁵ The mean carbon-carbon distance (1.393 Å) is similar to that observed in benzene¹⁵⁸ (1.398 Å) and in several di-substituted benzene compounds.¹⁵⁹ However in the benzene dithiol ligands in this structure there is a significant range of C-C distances (Fig. 10). In addition, these distances are consistent with a tendency towards the dithioketonic limit (Fig. 11). However caution must be used since the dithioketonic limit will not be attained due to other resonance

structures, so only a trend towards this limit is noted. Also due to increasing thermal motion of the carbon atoms as the distance from the central atom (Mo) increases, the bonds will appear shorter due to libration of the rings. Thus the shortening of $C_B - C_C$ (Fig. 10) could be partly attributed to thermal motion. However thermal motion of this type cannot cause bond lengthening, so the longer $C_A - C'_A$ bond remains as good evidence of the tendency of the ligand towards its oxidized formulation. At this point it is convenient to note that the thermal parameters in this and similar structures all show an anomalous feature. In molecules of this type it would appear reasonable to expect that the general trend of thermal amplitudes increases steadily as one progresses outward from the centre of gravity of the molecule. This assumes that the thermal motion is dominated by rigid body motion. However the sulfur atoms have larger thermal parameters than their attached carbon atoms. This observation, which appears to be very general for sulfur donor ligands, suggests either the unsuitability of the scattering factors used, or large vibration of the core of the molecule. This feature precludes any attempt at correction of these bond lengths for thermal motion and hence severely restricts the discussion

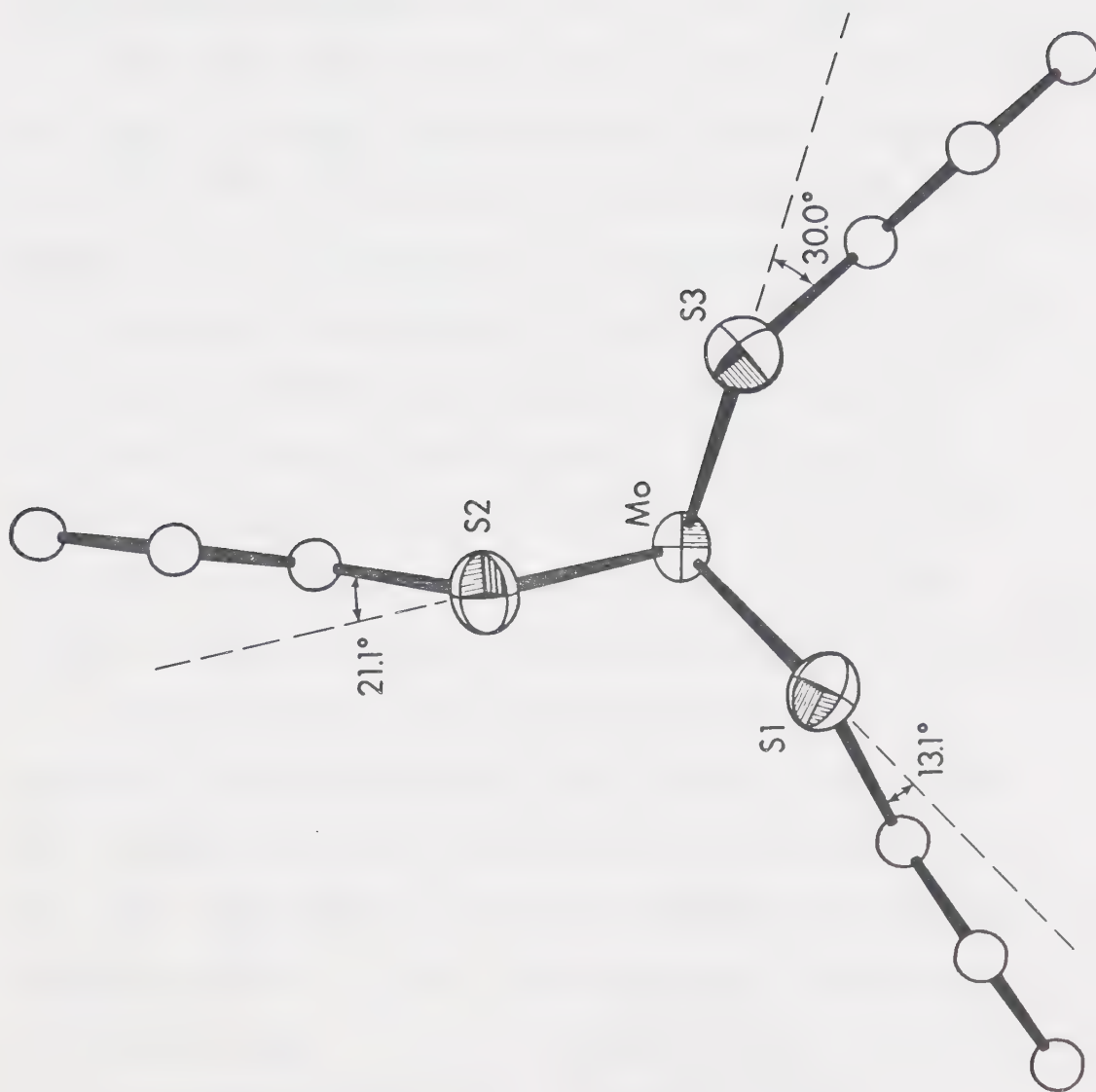


Fig. 12: VIEW OF $\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$ DOWN THE CRYSTALLOGRAPHIC c AXIS.

of the ligand geometry with respect to the pattern of carbon-carbon bond lengths. A more complete view of the ligand in its reduced and oxidized formulation is presented in Chapter IX, based on molecular orbital calculations performed by Birss and Das Gupta.¹⁶⁰

The mean S-M-S angle involving *trans* sulfur atoms is $136 \pm 1^\circ$ in the known trigonal prismatic structures,^{129,130,132} and assuming the constraint of ligand bite, has been calculated¹⁶¹ as approximately 173° in octahedral coordination. The mean value of 135.70° observed in $\text{Mo}(\text{bdt})_3$ is clearly consistent with trigonal prismatic coordination. The intra- and interligand S-Mo-S angles (82.12° and 81.53°) are similar, as expected, and again agree with those found in other trigonal prismatic structures.^{129,130,132}

As mentioned, the molecule deviates from D_{3h} symmetry due to the bend of the ligand planes from the respective S-Mo-S planes, as shown in Fig. 12, in which the molecule is viewed directly down the crystallographic *c* axis and approximate molecular three-fold axis. Similar bending of the ligand planes was observed in $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ ¹³⁰ and also in $\text{Mo}(\text{Se}_2\text{C}_2(\text{CF}_3)_2)_3$,¹⁵² where the ligand planes deviate from the MoS_2 and MoSe_2 planes by 18° and 18.6° respectively. Although these deviations are uniform

in these previous two examples, the molecules both having $3/m$ symmetry, they are irregular for $\text{Mo}(\text{bdt})_3$ with the ligand/ MoS_2 dihedral angles being 13.1° , 21.1° , and 30.0° (mean 21.4°). Schrauzer¹³⁰ has attributed this as being due to intramolecular effects, saying that the sulfur may be in a state between sp^2 and sp^3 hybridization, with possible added stabilization from packing forces. However from the structure of $\text{Mo}(\text{bdt})_3$ it is obvious that packing forces contribute significantly, as witnessed by the wide range in dihedral angles observed. Table 26 shows that several intermolecular contacts are comparable to the predicted van der Waals contacts¹⁵¹ (Predicted values: $\text{S}\cdots\text{C}$, 3.70 \AA ; $\text{S}\cdots\text{S}$, 3.70 \AA ; $\text{S}\cdots\text{H}$, 3.05 \AA ; $\text{C}\cdots\text{C}$, 3.70 \AA ; $\text{C}\cdots\text{H}$, 3.05 \AA ; $\text{H}\cdots\text{H}$, 2.40 \AA). Thus packing is very efficient and will probably be important in the bending of the ligand planes. A packing diagram, viewed down the c axis is shown in Fig. 13. The efficient packing is obvious from this diagram with the molecules packing in a gear-wheel arrangement.

As shown in Table 28, a further indication of the regularity of the prism is given by the similarity of the angles between the three MoS_2 planes, all being close to the expected value of 120° . The two tri-

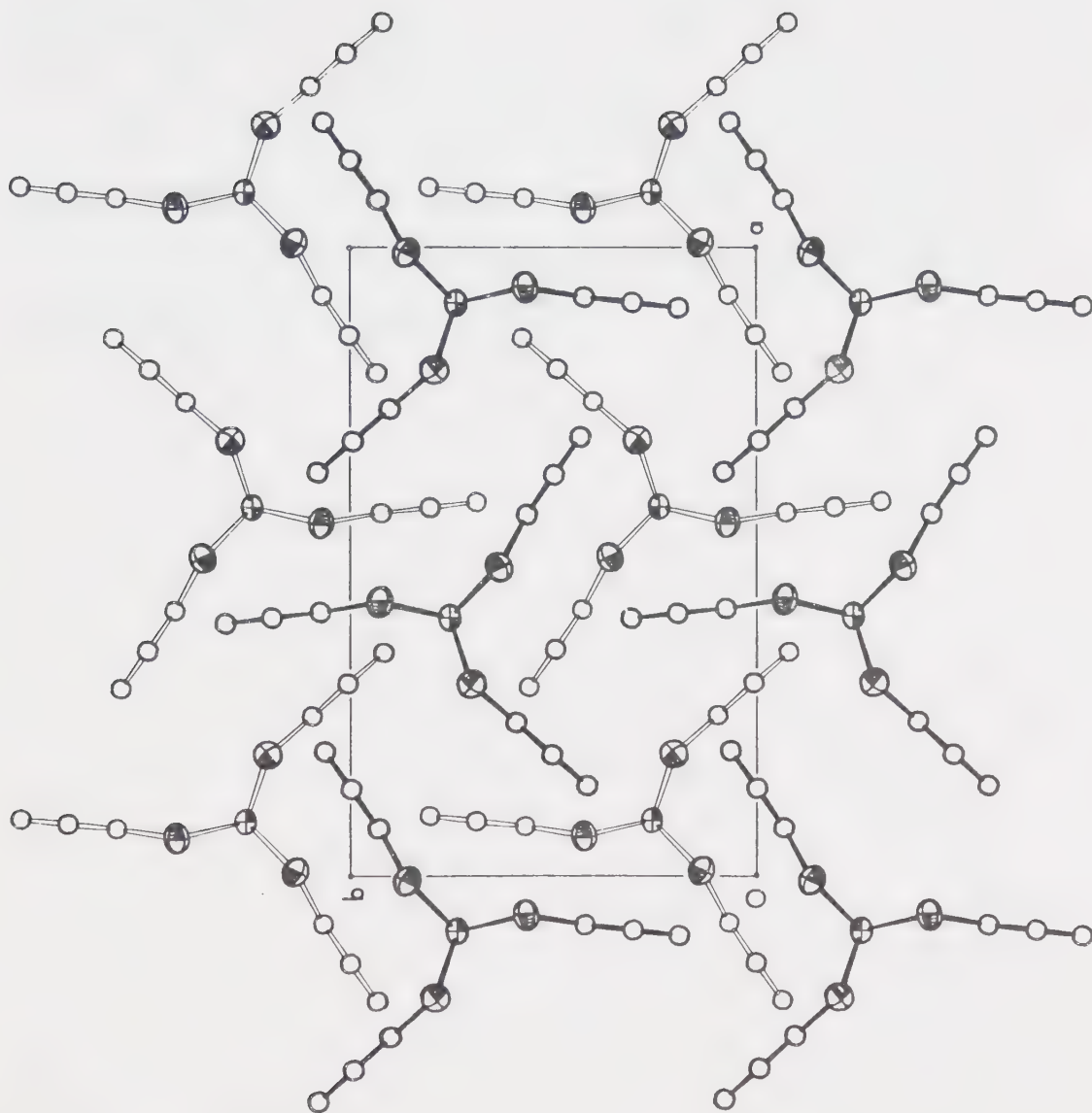


Fig. 13: PACKING DIAGRAM FOR $\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$, PROJECTED ON THE ab PLANE.

angular faces of the prism are also almost exactly parallel.

The Mo-S-C angles (mean 106.2°) are similar to the values of $109(1)^\circ$ and $109.9(4)^\circ$ observed in $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ and $\text{V}(\text{S}_2\text{C}_3\text{Ph}_2)_3$, however they are significantly smaller, again probably due to differences in the ligands. The S-C-C' angles (mean 119.4°) are in good agreement with the value of 120° . Similarly all C-C-C angles within the benzene rings are close to their expected value of 120° .

CHAPTER VII: THE CRYSTAL AND MOLECULAR STRUCTURE

OF TETRAPHENYLARSONIUM *TRIS* (BENZENE-
1,2-DITHIOLATO) NIOBIUM, $([(C_6H_5)_4As][Nb(S_2C_6H_4)])$

EXPERIMENTAL

Dark purple crystals suitable for single crystal X-ray diffraction study, prepared by the reaction of sodium cyclopentadienide with benzene dithiol and subsequent reaction with $Nb[N(CH_3)_2]_5$ and crystallization with tetraphenylarsonium chloride,¹⁴³ were kindly supplied by Dr. Takats and Mr. Martin. Preliminary photography indicated 2/m Laué symmetry consistent with a monoclinic space group. Systematic absences, as determined by Weissenberg ($h0\ell$, $h1\ell$; CuK_α X-radiation) and Precession photographs ($0k\ell$, $1k\ell$, $hk0$, hkl ; MoK_α X-radiation), are $0k0$: $k = 2n + 1$ and $h0\ell$: $h + \ell = 2n + 1$ indicating the non-standard space group $P2_1/n$, which was retained because of the convenient β angle. The cell parameters, obtained at 22°C from a least squares analysis of the setting angles of 12 reflections, which were centred accurately on a Picker automatic four circle diffractometer, using CuK_{α_1} X-radiation ($\lambda = 1.54051 \text{ \AA}$), are:
 $a = 22.983(7) \text{ \AA}$, $b = 12.747(4) \text{ \AA}$, $c = 13.150(3) \text{ \AA}$,
 $\beta = 92.09(2)^\circ$. The observed density, obtained by

floatation in aqueous zinc bromide solution, is $1.52(2)$ g cm^{-3} and is in reasonable agreement with the theoretical value of 1.54 g cm^{-3} calculated assuming four molecules with formula weight 896.94 a.m.u. per unit cell of volume 3867.12 \AA^3 .

Intensity data were collected on the Picker automatic diffractometer, using CuK_α X-radiation, filtered using a 0.0005" thick Ni foil, and using a 2° take-off angle. The crystal was aligned in a general orientation but with its b^* axis approximately coincident with the ϕ axis of the instrument. Crystal faces were identified and perpendicular distances between faces of the same form were measured as: $\{1,0,0\}$, 0.206 mm; $\{\bar{2},1,0\}$, 0.206 mm; $\{\bar{2},\bar{1},0\}$, 0.206 mm; $\{\bar{1},0,1\}$, 0.155 mm; $\{1,0,1\}$, 0.175 mm.

In the data collection a coupled $2\theta/\omega$ scan was used with a 2θ scan speed of $1^\circ/\text{min}$ to collect all reflections with $2\theta \leq 115^\circ$. The peak scan was 2° (2 min) for low angle reflections but increased with increasing 2θ due to compensation for $\alpha_1\alpha_2$ separation. Background counts were measured for 20 seconds at the limits of the two theta scan. The scattered X-rays were detected by a scintillation counter used in conjunction with a pulse height analyzer tuned to accept 95% of the CuK_α peak. Three standard reflections

were collected automatically every 100 data reflections. Another five standard reflections were collected manually every 10 hours to detect more precisely decomposition and crystal centering errors. No significant decomposition was observed but small fluctuations ($\pm 1\%$), due to an instability of the goniometer head, were detected. These fluctuations were not regular and corrections were not made.

Of the 5862 unique reflections collected, 3604 were considered as significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization and absorption effects. For CuK_{α} X-radiation, the linear absorption coefficient⁸⁶ is 68.42 cm^{-1} which yielded a range of transmission factors of 0.4359 to 0.3128. Standard deviations were estimated using a "p factor" of 0.03 as outlined in Chapter II. Terms used in the Zachariasen¹⁴⁸ extinction correction were calculated at this stage.

TABLE 29: MAJOR PATTERSON PEAKS AND THEIR ASSIGNMENT

OBSERVED VECTOR	RELATIVE INTENSITY	ASSIGNMENT	CALCULATED POSITION ^a
0.500, 0.063, 0.500	250	1/2, 1/2-2y ₁ , 1/2	0.500, 0.064, 0.500
0.339, 0.500, 0.106	226	1/2-2x ₁ , 1/2, 1/2-2z ₁	0.340, 0.500, 0.114
0.209, 0.377, 0.532	159	-(x ₁ +x ₂), (y ₁ +y ₂), -(z ₁ +z ₂)	0.208, 0.374, 0.544
0.287, 0.440, 0.958	148	1/2+(x ₁ +x ₂), 1/2-(y ₁ -y ₂), 1/2+(z ₁ +z ₂)	0.292, 0.438, 0.956
0.130, 0.126, 0.578	146	1/2-(x ₁ -x ₂), 1/2-(y ₁ +y ₂), 1/2-(z ₁ -z ₂)	0.132, 0.126, 0.570
0.500, 0.188, 0.500	140	1/2, 1/2-2y ₂ , 1/2	0.500, 0.188, 0.500
0.165, 0.424, 0.395	113	2x ₁ , 2y ₁ , 2z ₁	0.160, 0.436, 0.386
0.078, 0.500, 0.958	103	1/2-2x ₂ , 1/2, 1/2-2z ₂	0.076, 0.500, 0.974
0.418, 0.314, 0.532	63	2x ₂ , 2y ₂ , 2z ₂	0.424, 0.312, 0.526

^aCalculated on the basis of the consistent solution:

$$x_1 = 0.580, y_1 = 0.218, z_1 = 0.193; x_2 = 0.212, y_2 = 0.156, z_2 = 0.263.$$

STRUCTURE SOLUTION AND REFINEMENT

A sharpened¹⁴⁶ Patterson was calculated between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 1.0$. The general positions for space groups $P2_1/n$ are: x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $1/2 + x, 1/2 - y, 1/2 + z$; and $1/2 - x, 1/2 + y, 1/2 - z$. For one niobium [coordinates (x_1, y_1, z_1)] and one arsenic atom [coordinates (x_2, y_2, z_2)] per general position, the major peaks in the map can be assigned as shown in Table 29.

A brief outline of the refinement is shown in Table 30.

TABLE 30: REFINEMENT OUTLINE

MODEL	R_1	R_2
(1) Nb and As positions, B's fixed	0.421	0.507
(2) Nb, As, and S positions, isotropic B's	0.270	0.359
(3) Nb, As, S with isotropic B's, benzene rings as rigid bodies	0.076	0.087
(4) Absorption and Extinction ¹⁴⁷	0.064	0.072
(5) Nb, S, and As anisotropic	0.056	0.065
(6) Nb, S, and As anisotropic, ligand carbons individual isotropic, H atoms and benzene rings on arsenic as rigid bodies	0.049	0.051
(7) Model (6) but with anisotropic dithiolene carbons	0.047	0.048

Structure factors were calculated using the atomic scattering factors for the neutral atoms for niobium, arsenic, sulfur, and carbon as tabulated by Cromer and Mann.⁷⁵ The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.¹⁴⁹ In addition, anomalous dispersion corrections⁷⁶ were applied to the niobium, arsenic and sulfur scattering factors ($\Delta f'_{\text{Nb}} = -0.58$, $\Delta f''_{\text{Nb}} = 2.68$, $\Delta f'_{\text{As}} = -1.17$, $\Delta f''_{\text{As}} = 1.17$, $\Delta f'_{\text{S}} = 0.31$, $\Delta f''_{\text{S}} = 0.58$). Features surrounding the Nb, As and S atoms in the electron density difference map suggested the anisotropic refinement, and the validity was verified by a Hamilton's R Test⁷⁹ at the 0.005 significance level.

Initially the benzene rings were refined as rigid bodies constrained to their well known geometry. In model (6) the carbon atoms of the benzene dithiol ligands were refined individually with isotropic temperature factors, and the phenyl groups on the arsenic atoms were refined as rigid bodies. The hydrogen positions were calculated from the geometry and orientation of the benzene rings and were also added as rigid bodies, using a C-H distance of 1.0 Å. The hydrogen rigid bodies were not refined however. The final model was refined with anisotropic temperature factors on the carbon atoms of the dithiolene

ligands. This was again justified by a Hamilton's R Test⁷⁹ at the 0.005 significance level.

In the final least squares refinement, 284 parameters were varied, and the standard deviation in an observation of unit weight was 1.641. The final value of the refined extinction parameter, C , was 8.74×10^{-7} .

RESULTS

Observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 31. The final fractional coordinates and isotropic B's of all atoms are shown in Table 32. Standard deviations were obtained from the inverse matrix of the final least squares analysis. Table 33 shows the anisotropic thermal parameters (U_{ij} 's).⁸⁰ Intra-ionic contacts and angles, shown in Tables 34 and 35, were obtained with their standard deviations from ORFFE. Inter-ionic contacts (also obtained from ORFFE) are shown in Table 36. Selected least squares planes are given in Table 37. In Table 38, the dihedral angles between some selected planes are shown.

In Fig. 14 a three-dimensional view of the $\text{Nb}(\text{bdt})_3^-$ anion is shown. Fig. 16 shows the anion and the

$(\text{C}_6\text{H}_5)_4\text{As}^+$ cation together, viewed down the crystallographic b axis. The numbering scheme is shown in both diagrams. For the carbon atoms in the phenyl groups, the first number designates the ring number and the second number is the sequence of the atom in the ring. The carbon atoms are numbered sequentially and for the phenyl groups in the cation the first atom in the numbering scheme is always bonded to the arsenic atom. The hydrogen atoms are not shown but are numbered from H1 to H32 and are bonded, four on each dithiolene ligand and five on each phenyl group, sequentially from C12 to C76.

In the three dimensional representations the niobium, sulfur and arsenic atoms are shown with 50% probability thermal ellipsoids. The carbon atoms are shown, however, with artificially low isotropic thermal parameters, for clarity.

TABLE 31: OBSERVED AND CALCULATED STRUCTURE
FACTOR AMPLITUDES (ELECTRONS X 10)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 0*				-24	4	225	284	-18	8	281	254	-13	0	186	178	-4	2	474	465
-24	0	392	416	-22	4	425	428	-16	8	486	518	-12	0	332	347	-3	2	1266	1145
-22	0	258	305	-20	4	1304	1315	-14	8	254	240	-10	0	506	520	-2	2	1583	1514
-20	0	710	740	-14	4	436	441	-12	8	1570	1537	-9	0	698	715	-1	2	940	903
-18	0	825	793	-12	4	361	378	-8	8	307	287	-8	0	714	765	0	2	377	370
-14	0	1586	1593	-10	4	1648	1602	-6	8	1253	1312	-7	0	1381	1406	1	2	600	622
-12	0	601	595	-8	4	460	471	-2	8	1567	1593	-6	0	1944	2032	2	2	2044	2137
-10	0	1771	1779	-6	4	701	712	0	8	1366	1422	-4	0	895	876	3	2	231	256
-8	0	1451	1521	-4	4	798	708	2	8	1166	1158	-2	0	3003	3089	4	2	566	561
-6	0	177	177	-2	4	811	808	4	8	542	510	-1	0	229	254	5	2	263	266
-4	0	1442	1445	0	4	482	494	6	8	298	326	1	0	249	254	6	2	895	942
-2	0	150	190	2	4	504	535	8	8	1257	1296	2	0	3070	3089	7	2	264	287
2	0	136	190	4	4	940	965	10	8	220	229	4	0	891	876	8	2	642	671
4	0	1432	1445	6	4	799	891	12	8	712	709	6	0	1994	2032	10	2	963	1002
8	0	1475	1521	8	4	978	1046	14	8	273	243	7	0	1366	1406	12	2	769	820
10	0	1761	1779	10	4	743	813	18	8	795	760	8	0	728	765	13	2	275	214
12	0	609	595	12	4	388	384	20	8	300	318	9	0	708	715	14	2	188	132
14	0	1555	1593	14	4	1021	1058	-17	9	769	814	10	0	505	520	16	2	681	678
16	0	798	793	16	4	275	254	-15	9	404	401	12	0	319	347	18	2	561	578
20	0	729	740	20	4	933	923	-13	9	604	595	13	0	222	178	19	2	705	721
22	0	242	305	22	4	573	553	-9	9	1045	1046	14	0	485	487	20	2	422	382
24	0	381	416	-23	5	826	885	-7	9	319	366	15	0	235	244	22	2	493	497
-23	1	242	313	-21	5	246	239	-5	9	399	338	16	0	1176	1199	23	2	206	143
-21	1	997	1016	-19	5	358	388	-3	9	1204	1213	18	0	305	257	-23	3	408	380
-17	1	1234	1260	-17	5	231	254	-1	9	911	956	19	0	653	627	-21	3	1127	1139
-15	1	618	603	-13	5	705	644	1	9	845	845	22	0	519	570	-19	3	253	265
-13	1	943	991	-11	5	199	169	5	9	1517	1506	24	0	198	120	-18	3	365	318
-11	1	299	289	-9	5	1675	1573	7	9	351	355	-23	1	333	347	-17	3	439	438
-9	1	296	305	-7	5	1103	1042	9	9	289	289	-22	1	223	234	-16	3	575	537
-7	1	621	647	-5	5	571	563	15	9	901	885	-21	1	398	390	-15	3	358	373
-5	1	852	842	-3	5	341	351	17	9	236	225	-19	1	1257	1246	-14	3	260	264
-3	1	2846	2603	-1	5	239	225	19	9	210	200	-18	1	293	283	-13	3	398	380
-1	1	875	841	1	5	1375	1455	-12	10	485	549	-17	1	253	232	-12	3	184	84
1	1	1075	1239	3	5	2539	2662	-10	10	332	326	-16	1	665	687	-11	3	831	787
3	1	2074	2196	5	5	308	320	-8	10	603	608	-15	1	276	268	-9	3	850	826
5	1	3145	3123	7	5	699	740	-6	10	998	1051	-13	1	570	557	-8	3	923	910
7	1	1645	1683	9	5	353	400	-2	10	712	765	-11	1	1367	1369	-7	3	216	201
11	1	1822	1857	11	5	1034	1072	0	10	675	712	-10	1	1061	1036	-6	3	725	706
17	1	1490	1463	15	5	571	536	2	10	1381	1376	-9	1	395	400	-5	3	256	284
19	1	676	707	17	5	817	807	4	10	653	660	-8	1	562	549	-4	3	1281	1192
21	1	280	325	19	5	853	851	6	10	835	798	-7	1	220	211	-3	3	285	262
23	1	350	307	21	5	297	284	8	10	823	801	-5	1	856	916	-2	3	769	671
25	1	211	199	23	5	501	483	12	10	762	751	-4	1	473	468	-1	3	1214	1196
-24	2	566	591	-20	6	950	999	16	10	495	451	-3	1	334	341	0	3	1569	1518
-22	2	274	319	-18	6	380	367	-15	11	231	212	-2	1	1299	1209	1	3	2907	2826
-20	2	360	412	-16	6	532	541	-9	11	881	876	-1	1	1375	1221	2	3	2163	2226
-18	2	872	906	-14	6	218	254	-5	11	497	477	0	1	428	445	3	3	288	317
-16	2	655	625	-12	6	1225	1212	-1	11	399	374	1	1	2029	2240	4	3	252	260
-12	2	720	649	-10	6	1123	1167	1	11	599	542	2	1	653	704	5	3	1000	1061
-10	2	1514	1461	-8	6	509	491	9	11	595	576	3	1	1085	1139	6	3	314	333
-8	2	956	941	-6	6	929	927	11	11	754	811	4	1	174	216	8	3	500	528
-6	2	1294	1249	-4	6	321	312	13	11	264	270	5	1	1885	1918	9	3	1737	1795
-4	2	3766	3379	-2	6	902	943	15	11	483	495	6	1	299	294	10	3	329	312
-2	2	2442	2278	0	6	485	436	-10	12	289	311	7	1	869	909	11	3	958	952
0	2	2486	2421	2	6	848	852	-8	12	280	304	9	1	1626	1699	12	3	633	625
2	2	278	315	4	6	619	627	-6	12	962	1020	10	1	1062	1104	13	3	695	719
4	2	772	770	6	6	352	345	-2	12	221	157	11	1	479	552	14	3	510	528
6	2	1700	1764	10	6	1005	999	4	12	860	925	12	1	289	285	15	3	404	413
8	2	1439	1492	12	6	851	890	6	12	382	356	13	1	923	941	16	3	266	208
12	2	571	594	14	6	538	539	8	12	1028	1048	14	1	658	655	17	3	454	462
14	2	1566	1637	18	6	383	368	10	12	254	197	15	1	305	333	19	3	767	768
18	2	242	288	20	6	570	589	12	12	340	345	16	1	861	885	21	3	302	315
20	2	966	997	22	6	738	719	-9	13	590	603	17	1	243	293	22	3	303	252
24	2	371	375	-21	7	281	327	-5	13	592	633	19	1	1144	1146	-24	4	414	438
-23	3	910	909	-19	7	633	596	-1	13	226	248	21	1	228	193	-23	4	293	268
-21	3	580	554	-17	7	773	791	1	13	203	159	22	1	255	283	-22	4	269	250
-19	3	566	525	-15	7	739	726	3	13	549	591	-24	2	309	307	-21	4	280	257
-15	3	525	528	-13	7	597	604	5	13	638	643	-23	2	203	158	-19	4	312	280
-13	3	453	446	-9	7	1301	1308	7	13	430	438	-21	2	302	312	-16	4	803	825
-11	3	495	503	-7	7	832	833	-6	14	337	268	-20	2	305	307	-16	4	289	270
-9	3	443	332	-5	7	858	844	-2	14	215	238	-19	2	457	440	-14	4	469	476
-7	3	2384	2290	-3	7	1385	1365	2	14	618	622	-18	2	477	482	-13	4	784	796
-5	3	2812	2643	1	7	2691	2655	4	14	618	622	-16	2	606	587	-12	4	371	385
-3	3	1367	1267	3	7	889	857	-24	0	199	120	-14	2	355	369	-11	4	207	232
-1	3	815	776	5	7	1235	1210	-22	0	568	570	-13	2	511	479	-9	4	647	624
1	3	792	853	7	7	660	690	-21	0	225	197	-12	2	545	544	-8	4	1256	1233
3	3	1740	1918	9	7	796	795	-19	0	621	627	-10	2	215	192	-7	4	1243	1206
7	3	762	812	11	7	218	246	-18	0	277	257	-8	2	1793	1653	-6	4	164	120
11	3	1404	1476	15	7	1095	1043	-16	0	1167	1199	-7	2	700	704	-5	4	448	440
15	3	652	754	19	7	414	413	-15	0	241	244	-6	2	548	536	-4	4	885	856

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 1*				14	6	458	421	2	9	367	403	-13	0	1290	1294	-15	2	451	466
-2	4	557	545	17	6	331	378	3	9	449	465	-12	0	978	985	-14	2	190	204
-1	4	1372	1341	18	6	426	462	7	9	934	965	-11	0	471	460	-13	2	670	659
0	4	250	224	21	6	825	804	12	9	344	308	-10	0	1501	1478	-12	2	492	503
1	4	1212	1245	22	6	295	303	13	9	719	742	-9	0	533	581	-11	2	1096	1083
2	4	1786	1820	-21	7	578	600	14	9	257	251	-8	0	1617	1622	-10	2	1593	1568
6	4	1503	1570	-19	7	389	384	16	9	465	447	-7	0	502	487	-9	2	337	341
7	4	397	386	-15	7	981	988	17	9	328	353	-6	0	1144	1179	-7	2	925	980
8	4	518	509	-14	7	238	215	-18	10	228	190	-5	0	844	872	-6	2	871	905
9	4	1019	1063	-13	7	493	533	-15	10	318	298	-4	0	1705	1676	-4	2	1961	1797
11	4	190	198	-11	7	556	541	-14	10	567	636	-3	0	1492	1508	-3	2	2767	2514
12	4	586	1011	-10	7	586	575	-11	10	209	233	-2	0	1043	1033	-2	2	1123	1062
13	4	716	719	-9	7	850	836	-8	10	475	463	-1	0	265	282	0	2	444	465
14	4	252	260	-7	7	1510	1485	-6	10	275	287	0	0	2940	2998	1	2	294	341
15	4	204	204	-6	7	196	152	-4	10	712	694	1	0	254	282	2	2	426	466
16	4	625	647	-5	7	585	568	-3	10	385	385	2	0	1026	1033	3	2	1270	1371
17	4	272	264	-4	7	431	449	-2	10	415	397	3	0	1514	1508	4	2	598	665
18	4	310	253	-3	7	232	257	-1	10	469	486	4	0	1676	1676	5	2	863	903
19	4	222	256	-2	7	578	605	0	10	536	537	5	0	878	672	6	2	985	1040
20	4	509	500	-1	7	2165	2142	2	10	1022	1031	6	0	1161	1179	7	2	611	604
22	4	871	863	0	7	228	219	3	10	209	199	7	0	508	487	8	2	2114	2174
-23	5	209	226	1	7	257	276	4	10	361	357	8	0	1599	1622	10	2	557	548
-21	5	686	677	2	7	599	617	5	10	224	213	9	0	538	581	11	2	258	263
-18	5	367	378	3	7	789	791	6	10	593	560	10	0	1487	1478	12	2	454	474
-16	5	424	460	4	7	197	171	10	10	982	962	11	0	457	460	13	2	502	513
-15	5	795	778	5	7	225	251	13	10	370	379	12	0	947	985	14	2	383	405
-12	5	308	262	7	7	951	948	16	10	387	375	13	0	1270	1294	17	2	845	889
-11	5	335	306	8	7	228	238	17	10	326	282	14	0	672	699	20	2	574	579
-10	5	298	228	9	7	950	931	-14	11	231	227	15	0	595	603	21	2	288	277
-9	5	741	723	10	7	222	235	-11	11	769	760	17	0	529	549	-24	3	614	666
-8	5	362	361	11	7	562	582	-8	11	530	596	18	0	316	347	-23	3	314	354
-7	5	642	600	12	7	408	433	-7	11	493	545	20	0	387	409	-21	3	330	365
-6	5	479	470	13	7	325	309	-6	11	539	598	21	0	508	539	-20	3	250	220
-5	5	1105	1077	14	7	246	228	-5	11	220	218	24	0	282	291	-19	3	483	502
-4	5	1341	1271	15	7	241	189	-4	11	427	467	-24	1	389	442	-18	3	318	336
-3	5	157	167	17	7	728	702	-3	11	690	725	-21	1	638	664	-16	3	236	264
-2	5	913	882	20	7	251	178	-1	11	361	403	-18	1	326	332	-14	3	857	874
-1	5	1209	1222	-18	8	892	925	0	11	274	211	-16	1	556	580	-13	3	576	937
0	5	316	295	-16	8	457	410	1	11	317	294	-15	1	589	576	-12	3	270	249
1	5	1543	1546	-14	8	818	809	4	11	230	219	-14	1	520	510	-11	3	715	690
2	5	318	297	-13	8	421	487	5	11	382	364	-13	1	1330	1355	-10	3	1504	1452
3	5	961	993	-12	8	634	616	6	11	237	263	-12	1	692	652	-9	3	1545	1393
5	5	675	652	-11	8	269	286	7	11	992	967	-11	1	708	697	-7	3	880	872
6	5	1281	1276	-10	8	754	738	9	11	544	551	-10	1	484	515	-6	3	205	224
9	5	2060	2030	-9	8	241	254	10	11	462	362	-9	1	1625	1594	-4	3	2231	2045
10	5	897	939	-8	8	412	351	11	11	229	136	-8	1	381	365	-3	3	1107	1040
13	5	344	312	-6	8	299	272	13	11	614	627	-7	1	726	728	-2	3	1970	1862
14	5	522	569	-5	8	698	722	-14	12	203	233	-5	1	248	241	-1	3	536	528
15	5	316	320	-4	8	1452	1438	-11	12	400	413	-4	1	1704	1625	0	3	877	874
17	5	447	450	-3	8	470	460	-8	12	563	584	-3	1	1340	1260	1	3	863	883
19	5	704	696	-2	8	632	616	-6	12	484	511	-2	1	1706	1633	2	3	330	356
21	5	530	562	-1	8	594	611	-3	12	391	398	-1	1	1188	1114	3	3	745	795
22	5	287	239	2	8	1674	1703	0	12	384	428	0	1	2069	2080	4	3	605	649
23	5	427	422	3	8	410	389	1	12	312	295	1	1	255	264	5	3	227	255
-22	6	321	322	4	8	798	800	2	12	373	381	2	1	269	342	6	3	444	458
-20	6	211	198	5	8	630	638	4	12	463	451	3	1	3026	3179	7	3	1318	1375
-18	6	1144	1132	6	8	377	367	6	12	294	255	4	1	1506	1550	8	3	1466	1491
-14	6	343	344	7	8	204	216	10	12	800	803	5	1	711	758	9	3	200	174
-12	6	1076	1071	9	8	200	200	11	12	546	509	6	1	1432	1488	10	3	540	520
-11	6	305	253	10	8	929	975	12	12	270	272	7	1	690	712	11	3	1429	1478
-10	6	847	792	12	8	623	836	-11	13	613	656	8	1	842	885	12	3	1292	1311
-9	6	387	367	13	8	429	437	-9	13	253	292	9	1	543	573	13	3	375	371
-8	6	843	825	14	8	491	489	-8	13	212	265	10	1	1334	1393	14	3	940	950
-7	6	846	776	15	8	411	405	-6	13	498	526	11	1	1477	1476	17	3	543	571
-5	6	682	649	16	8	657	611	-3	13	557	560	12	1	271	244	19	3	340	289
-4	6	2036	1924	17	8	519	479	-1	13	301	313	13	1	462	498	22	3	249	137
-3	6	357	318	18	8	355	298	1	13	315	359	14	1	946	961	23	3	351	342
-2	6	703	649	20	8	521	506	3	13	625	624	16	1	729	763	24	3	328	372
-1	6	486	464	-19	9	477	521	7	13	275	281	17	1	477	447	-23	4	277	309
0	6	497	544	-18	9	265	234	8	13	354	325	18	1	424	468	-22	4	232	245
1	6	483	499	-17	9	327	339	9	13	456	438	19	1	321	360	-21	4	539	535
2	6	470	476	-15	9	220	291	-6	14	342	374	20	1	395	377	-20	4	524	534
3	6	427	415	-14	9	434	412	0	14	694	688	21	1	592	581	-18	4	220	202
4	6	410	403	-13	9	318	326	***K = 2****				22	1	217	165	-16	4	410	395
5	6	406	411	-12	9	229	160	-24	0	321	291	24	1	243	231	-15	4	523	503
6	6	1072	1095	-11	9	1115	1132	-21	0	553	539	-24	2	327	364	-14	4	601	570
7	6	347	328	-10	9	332	341	-20	0	375	400	-22	2	244	234	-13	4	944	929
8	6	740	767	-7	9	860	888	-18	0	345	347	-21	2	536	528	-12	4	312	269
9	6	286	273	-4	9	739	731	-17	0	545	549	-18	2	557	580	-11	4	983	928
10	6	533	566	-2	9	467	466	-15	0	617	603	-17	2	225	166	-10	4	1498	1460
12	6	834	861	-1	9	1													

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 2**																			
-8	4	359	327	6	6	419	421	-9	9	925	902	8	13	562	552	-13	2	886	856
-7	4	2817	2643	7	6	886	881	-8	9	865	912	-5	14	540	544	-12	2	1043	1029
-5	4	1647	1628	8	6	646	639	-7	9	242	197	-2	14	495	541	-10	2	885	849
-4	4	1037	966	9	6	419	445	-4	9	778	777	2	14	559	575	-8	2	644	637
-3	4	561	521	10	6	989	1033	-3	9	588	617	**K = 3****				-7	2	455	424
-2	4	737	727	11	6	256	221	-2	9	942	918	-22	0	345	319	-6	2	466	428
-1	4	662	651	12	6	491	522	-1	9	670	677	-20	0	682	696	-5	2	1676	1641
0	4	508	495	13	6	414	406	1	9	599	611	-19	0	496	485	-4	2	682	646
1	4	1606	1607	14	6	298	307	2	9	685	676	-18	0	250	195	-3	2	323	281
2	4	387	395	15	6	665	688	3	9	501	493	-16	0	208	144	-2	2	146	168
3	4	1315	1375	16	6	298	283	4	9	577	584	-15	0	724	727	-1	2	854	812
4	4	1355	1379	17	6	493	468	5	9	782	783	-14	0	559	552	0	2	1741	1718
5	4	799	822	18	6	416	381	6	9	765	774	-13	0	455	448	1	2	307	335
7	4	854	887	22	6	528	524	7	9	204	203	-11	0	1145	1151	2	2	797	846
8	4	769	817	-21	7	261	250	9	9	526	534	-10	0	1435	1455	3	2	497	514
9	4	830	920	-20	7	301	270	10	9	562	555	-8	0	991	1009	4	2	780	852
11	4	389	427	-17	7	407	388	12	9	585	550	-7	0	1113	1086	5	2	838	907
12	4	328	374	-15	7	492	490	15	9	221	236	-6	0	207	149	6	2	600	615
14	4	604	597	-13	7	367	328	16	9	778	169	-5	0	710	727	7	2	307	313
15	4	1098	1126	-12	7	611	600	18	9	712	678	-4	0	357	329	9	2	910	944
16	4	433	382	-11	7	523	504	-17	10	227	257	-3	0	1633	1657	10	2	1291	1358
17	4	254	172	-9	7	721	711	-16	10	236	219	-2	0	726	723	11	2	347	380
18	4	282	284	-8	7	1070	1054	-12	10	833	838	-1	0	308	345	13	2	370	438
19	4	311	259	-7	7	766	782	-9	10	594	646	1	0	304	345	14	2	397	425
20	4	565	580	-6	7	438	436	-3	10	387	395	2	0	726	723	15	2	253	246
21	4	290	223	-5	7	959	904	0	10	507	540	3	0	1628	1657	16	2	283	322
22	4	398	395	-4	7	663	660	1	10	560	582	4	0	334	329	17	2	404	390
-23	5	232	269	-3	7	578	598	2	10	801	797	5	0	725	727	18	2	367	380
-20	5	539	540	-2	7	519	525	3	10	261	245	7	0	1106	1086	19	2	580	598
-19	5	338	343	-1	7	687	679	5	10	472	457	8	0	989	1009	20	2	285	297
-18	5	217	232	0	7	327	353	7	10	493	540	10	0	1415	1455	22	2	444	446
-17	5	300	277	1	7	664	685	8	10	542	532	11	0	1110	1151	24	2	227	209
-16	5	238	204	3	7	287	332	9	10	277	274	13	0	452	448	-22	3	324	278
-15	5	379	417	4	7	378	381	10	10	242	200	14	0	550	552	-19	3	424	430
-14	5	400	409	6	7	307	309	12	10	410	427	15	0	713	727	-18	3	569	557
-13	5	811	792	7	7	1160	1165	15	10	862	791	19	0	490	485	-17	3	657	611
-12	5	294	288	8	7	259	191	16	10	303	261	20	0	689	696	-16	3	642	662
-11	5	691	683	9	7	777	777	-13	11	344	395	22	0	318	319	-15	3	622	599
-10	5	1553	1472	11	7	256	248	-12	11	410	419	-23	1	255	292	-14	3	540	559
-8	5	1058	959	13	7	281	286	-9	11	574	604	-22	1	203	243	-12	3	408	413
-7	5	504	469	14	7	583	597	-8	11	453	461	-19	1	318	270	-11	3	841	826
-6	5	1075	1078	15	7	383	425	-6	11	824	808	-18	1	628	632	-9	3	739	715
-5	5	534	468	16	7	239	252	-5	11	281	212	-17	1	283	262	-8	3	1977	1865
-4	5	861	820	17	7	249	254	-4	11	270	306	-16	1	783	775	-7	3	771	732
-3	5	441	429	18	7	483	452	-2	11	303	335	-14	1	441	489	-6	3	387	384
-2	5	1232	1210	21	7	439	441	-1	11	468	489	-13	1	198	162	-5	3	747	734
-1	5	1036	976	-21	8	240	210	0	11	280	275	-12	1	177	159	-4	3	761	740
0	5	194	225	-20	8	437	448	2	11	527	535	-11	1	1435	1444	-3	3	335	353
1	5	1637	1620	-18	8	226	253	3	11	331	272	-10	1	279	279	-2	3	789	772
3	5	365	361	-17	8	345	354	4	11	375	353	-8	1	1226	1179	-1	3	309	293
4	5	1158	1210	-15	8	701	735	5	11	581	574	-7	1	958	944	0	3	760	736
7	5	662	699	-14	8	360	365	7	11	240	225	-6	1	908	890	1	3	742	717
9	5	462	435	-13	8	355	361	8	11	457	486	-5	1	402	395	2	3	494	496
10	5	804	818	-12	8	815	811	9	11	325	303	-4	1	540	527	3	3	911	991
11	5	1446	1473	-11	8	947	947	10	11	280	274	-3	1	1241	1189	4	3	399	450
12	5	1598	1608	-10	8	720	705	11	11	257	230	-2	1	379	412	5	3	867	925
13	5	250	226	-8	8	716	690	12	11	257	274	-1	1	1376	1290	6	3	2526	2671
16	5	457	454	-7	8	671	660	-13	12	246	257	1	1	1595	1691	7	3	168	157
19	5	355	426	-6	8	402	413	-12	12	238	313	2	1	208	192	8	3	1140	1133
21	5	252	257	-4	8	672	612	-9	12	533	562	3	1	428	448	9	3	630	701
22	5	369	331	-2	8	386	387	-7	12	420	438	4	1	431	457	10	3	363	346
-20	6	660	679	0	8	959	952	-6	12	231	244	6	1	1045	1063	12	3	885	958
-16	6	280	291	1	8	990	982	-5	12	669	718	7	1	1227	1333	13	3	905	953
-14	6	631	575	2	8	306	317	-4	12	288	322	8	1	1066	1104	14	3	281	273
-13	6	666	683	3	8	268	291	-2	12	471	479	9	1	693	712	15	3	360	319
-12	6	638	622	4	8	828	815	0	12	324	293	10	1	772	764	16	3	445	494
-11	6	319	316	5	8	622	643	2	12	435	473	11	1	433	448	18	3	358	363
-10	6	1077	1032	6	8	507	510	5	12	451	407	12	1	686	709	20	3	408	413
-9	6	1360	1307	7	8	433	420	6	12	240	245	13	1	285	261	22	3	549	542
-8	6	469	428	8	8	497	520	8	12	524	535	14	1	740	734	-23	4	308	338
-7	6	656	655	9	8	392	380	12	12	331	322	16	1	1316	1303	-21	4	310	322
-5	6	201	151	10	8	523	523	-10	13	202	194	17	1	395	398	-20	4	513	476
-4	6	182	184	11	8	615	577	-9	13	299	338	18	1	356	347	-19	4	301	324
-3	6	376	340	12	8	485	463	-8	13	702	715	19	1	310	246	-18	4	482	502
-2	6	1028	1039	13	8	527	553	-7	13	194	211	22	1	457	431	-17	4	355	381
-1	6	158	152	15	8	983	1000	-2	13	352	390	-20	2	555	571	-15	4	1173	1144
0	6	351	360	17	8	346	324	-1	13	331	370	-19	2	540	549	-14	4	488	488
1	6	1097	1095	18	8	503	463	1	13	295	297	-17	2	386	400	-13	4	893	890
2	6	244	251	20	8	273	285	5	13	460	468	-15	2	710	708	-12	4	1109	1065
3	6	445	452	-19	9	295	233												

Table 31 (continued)

M	L	FOBS	FCAL	M	L	FOBS	FCAL	M	L	FOBS	FCAL	M	L	FOBS	FCAL	M	L	FOBS	FCAL
K = 3**				2	6	1069	1047	3	9	261	235	-24	0	324	353	-10	2	507	499
-9	4	939	894	3	6	224	266	4	9	489	495	-23	0	199	145	-9	2	361	366
-8	4	1350	1272	4	6	451	400	5	9	867	858	-22	0	479	500	-8	2	416	413
-7	4	1202	1156	5	6	430	443	6	9	378	353	-21	0	287	340	-7	2	833	803
-6	4	613	575	6	6	604	620	7	9	575	569	-18	0	344	321	-6	2	250	243
-5	4	1960	1883	7	6	567	559	10	9	537	518	-15	0	337	375	-5	2	183	142
-4	4	888	825	8	6	1033	1047	11	9	420	467	-14	0	332	379	-4	2	857	836
-3	4	635	602	9	6	1189	1210	12	9	549	543	-13	0	646	653	-3	2	1866	1741
-2	4	885	870	12	6	689	725	14	9	440	445	-12	0	779	785	-2	2	170	157
-1	4	639	641	13	6	585	570	16	9	419	433	-11	0	800	793	-1	2	655	652
0	4	1815	1818	14	6	242	261	-17	10	304	306	-10	0	218	216	1	2	931	942
1	4	264	237	17	6	442	428	-16	10	368	364	-9	0	344	365	2	2	944	1027
2	4	1063	1087	19	6	253	209	-15	10	424	453	-7	0	970	936	3	2	1400	1480
3	4	1206	1252	20	6	377	348	-14	10	387	420	-5	0	338	344	4	2	547	556
4	4	163	145	21	6	372	349	-13	10	221	272	-4	0	1839	1879	5	2	1365	1415
6	4	804	810	-20	7	356	324	-12	10	326	285	-2	0	1436	1393	6	2	303	315
7	4	419	418	-19	7	376	350	-11	10	616	630	-1	0	255	207	7	2	313	328
8	4	234	243	-18	7	212	225	-10	10	474	510	0	0	556	545	8	2	288	275
9	4	1450	1488	-14	7	678	708	-9	10	226	147	1	0	208	207	10	2	1216	1217
10	4	721	721	-13	7	480	520	-8	10	407	419	2	0	1405	1393	11	2	963	995
11	4	489	453	-12	7	256	254	-7	10	445	441	4	0	1807	1879	12	2	643	664
12	4	267	205	-11	7	215	258	-3	10	420	437	5	0	349	344	13	2	506	506
13	4	301	344	-9	7	869	814	-2	10	547	533	6	0	206	73	14	2	381	384
15	4	347	377	-8	7	408	439	-1	10	671	675	7	0	962	936	15	2	475	491
16	4	330	350	-7	7	698	684	2	10	418	418	9	0	335	365	16	2	312	296
17	4	469	456	-6	7	225	186	3	10	408	395	10	0	181	216	17	2	397	381
18	4	280	315	-5	7	414	417	4	10	606	608	11	0	774	793	18	2	378	404
19	4	280	243	-4	7	675	651	5	10	301	251	12	0	743	785	19	2	334	328
20	4	572	578	-3	7	272	274	7	10	860	821	13	0	627	653	20	2	659	670
23	4	428	410	-2	7	1162	1155	8	10	367	375	14	0	354	379	21	2	234	204
-21	5	257	249	-1	7	630	590	9	10	535	514	15	0	362	375	23	2	260	296
-18	5	540	531	1	7	157	140	10	10	578	571	18	0	367	321	-23	3	211	207
-17	5	396	407	2	7	746	743	13	10	384	401	21	0	334	340	-21	3	356	361
-15	5	494	456	3	7	442	474	16	10	247	210	22	0	482	500	-19	3	625	625
-13	5	630	622	4	7	356	340	-15	11	256	241	24	0	332	354	-18	3	526	506
-12	5	1015	992	5	7	774	792	-14	11	781	832	-24	1	566	570	-17	3	333	339
-11	5	451	414	6	7	822	796	-12	11	244	277	-21	1	431	392	-16	3	626	621
-9	5	663	667	8	7	199	191	-11	11	387	399	-19	1	737	732	-15	3	693	674
-8	5	873	857	9	7	795	775	-10	11	265	247	-17	1	304	329	-13	3	374	371
-7	5	393	414	10	7	292	301	-8	11	557	555	-16	1	490	511	-12	3	439	398
-6	5	642	640	11	7	807	829	-7	11	233	225	-15	1	382	343	-11	3	858	882
-5	5	160	153	12	7	728	725	-6	11	609	661	-14	1	816	798	-10	3	1056	1017
-4	5	2130	1972	14	7	256	251	-5	11	263	250	-12	1	446	411	-9	3	977	948
-3	5	1728	1598	17	7	348	368	-4	11	370	349	-11	1	246	270	-8	3	561	474
-2	5	939	908	19	7	457	413	-3	11	381	390	-10	1	1034	1013	-6	3	1115	1005
-1	5	839	858	20	7	360	343	0	11	954	925	-9	1	1278	1285	-5	3	328	307
1	5	626	611	-20	8	262	337	1	11	831	790	-7	1	768	749	-4	3	793	784
2	5	637	634	-18	8	232	158	2	11	329	294	-6	1	1218	1215	-3	3	223	187
3	5	933	996	-17	8	508	561	4	11	482	522	-5	1	395	412	-1	3	2527	2436
5	5	1215	1232	-15	8	225	240	7	11	500	476	-4	1	869	835	0	3	563	559
6	5	2240	2293	-12	8	223	204	10	11	432	436	-3	1	561	523	1	3	517	517
7	5	195	203	-10	8	940	986	-12	12	481	537	-2	1	374	330	2	3	855	873
8	5	261	283	-9	8	236	185	-11	12	625	657	-1	1	913	820	3	3	453	454
9	5	655	683	-5	8	715	757	-9	12	266	278	0	1	645	640	4	3	1880	1908
10	5	516	509	-2	8	570	545	-8	12	225	196	1	1	1061	1109	5	3	813	852
11	5	456	428	-1	8	928	923	-7	12	209	198	2	1	480	479	6	3	878	899
12	5	491	502	2	8	648	653	-5	12	233	233	3	1	292	317	7	3	580	573
13	5	636	691	5	8	615	615	-3	12	684	712	4	1	807	836	8	3	1100	1153
14	5	338	324	6	8	218	275	-2	12	743	779	5	1	581	596	9	3	374	394
16	5	236	154	8	8	1111	1117	0	12	545	559	6	1	1556	1651	11	3	198	170
17	5	419	399	9	8	1049	1064	2	12	355	278	7	1	780	770	12	3	215	181
18	5	309	328	10	8	331	307	3	12	566	589	8	1	722	739	13	3	499	470
19	5	347	364	12	8	296	277	4	12	356	408	9	1	1194	1220	14	3	1155	1137
20	5	586	587	13	8	489	445	6	12	307	297	10	1	622	648	15	3	386	402
21	5	400	397	14	8	330	322	7	12	503	490	12	1	219	207	19	3	491	490
-22	6	329	338	15	8	225	280	11	12	497	502	14	1	812	816	22	3	345	327
-18	6	503	464	16	8	257	178	-8	13	305	351	15	1	619	626	23	3	219	216
-17	6	409	410	17	8	488	435	-6	13	457	493	16	1	927	942	-22	4	285	322
-15	6	744	753	-19	9	441	487	-4	13	267	247	18	1	375	327	-21	4	366	396
-14	6	248	245	-18	9	304	318	-3	13	468	456	19	1	451	454	-20	4	277	345
-13	6	232	214	-15	9	209	220	-2	13	261	282	20	1	361	411	-19	4	364	319
-12	6	988	963	-14	9	806	849	-1	13	248	286	21	1	753	766	-18	4	703	695
-10	6	613	591	-13	9	621	604	0	13	462	479	22	1	292	251	-17	4	709	702
-8	6	1041	978	-12	9	522	516	1	13	348	334	23	1	486	509	-16	4	703	704
-7	6	392	414	-9	9	357	312	3	13	520	505	-22	2	275	328	-14	4	873	867
-6	6	444	447	-8	9	220	108	5	13	345	366	-18	2	497	517	-13	4	1387	1369
-5	6	919	882	-5	9	358	339	6	13	274	243	-15	2	208	206	-12	4	206	215
-3	6	390	359	-4	9	746	772	-1	14	182	98	-14	2	645	657	-8	4	346	323
-2	6	298	298	-2	9	489	483	0	14	484	484	-13	2	1335	1353	-7	4	1843	1728
-1	6	1121	1141	-1	9	260	255	1	14	246	302	-12	2	980	982	-6	4	919	875
0	6	510	523	1	9	262	265	**K = 4****				-11	2						

Table 31 (continued)

M	L	FOBS	FCAL	M	L	FOBS	FCAL	M	L	FOBS	FCAL	M	L	FOBS	FCAL	M	L	FOBS	FCAL
K = 4**				17	6	372	382	-4	10	526	546	16	0	523	540	-11	3	350	354
-4	4	1769	1702	18	6	348	279	-3	10	410	405	17	0	275	241	-9	3	576	539
-3	4	998	927	21	6	303	263	0	10	439	417	18	0	235	275	-8	3	393	404
-2	4	961	964	-21	7	540	581	1	10	297	315	19	0	243	206	-7	3	1181	1136
-1	4	662	621	-20	7	251	291	2	10	277	202	20	0	677	721	-6	3	530	507
0	4	240	250	-18	7	307	370	3	10	629	591	-23	1	346	361	-4	3	1107	1047
1	4	1478	1490	-17	7	212	175	5	10	736	762	-22	1	256	272	-3	3	2155	2030
2	4	1908	1855	-14	7	426	480	6	10	541	555	-17	1	678	660	-2	3	845	807
4	4	876	915	-13	7	259	176	7	10	484	489	-16	1	328	315	-1	3	317	288
5	4	500	535	-12	7	515	506	8	10	269	252	-15	1	732	729	0	3	1413	1401
6	4	1507	1535	-11	7	766	736	9	10	288	347	-14	1	475	486	1	3	861	887
7	4	1442	1463	-10	7	442	451	12	10	210	176	-13	1	284	311	3	3	298	326
8	4	215	212	-9	7	253	232	14	10	259	232	-12	1	404	386	4	3	543	624
9	4	251	240	-7	7	289	319	15	10	456	455	-10	1	779	770	5	3	343	342
10	4	619	640	-6	7	609	618	-15	11	364	391	-8	1	1083	1079	6	3	950	976
11	4	1053	1092	-5	7	741	734	-14	11	213	170	-7	1	1140	1153	7	3	287	306
12	4	432	454	-4	7	409	365	-13	11	419	453	-6	1	636	642	8	3	353	384
14	4	388	371	-3	7	534	540	-12	11	638	669	-5	1	937	940	9	3	301	335
15	4	565	586	2	7	661	694	-8	11	270	303	-4	1	947	919	10	3	195	200
16	4	586	981	4	7	858	879	-7	11	323	339	-3	1	1923	1841	11	3	380	353
17	4	442	438	5	7	834	830	-6	11	536	560	-2	1	331	357	12	3	909	929
18	4	464	417	6	7	276	266	-5	11	232	240	0	1	157	91	13	3	274	257
19	4	244	207	7	7	584	556	-4	11	300	328	2	1	1077	1153	14	3	251	211
21	4	218	204	8	7	444	420	-3	11	292	292	3	1	924	1024	15	3	417	424
-20	5	323	371	9	7	605	639	-1	11	609	602	4	1	718	743	16	3	980	966
-19	5	538	527	12	7	340	289	1	11	219	156	6	1	931	950	21	3	320	283
-16	5	358	281	13	7	556	575	2	11	944	946	7	1	538	573	22	3	239	326
-15	5	215	182	17	7	290	329	3	11	279	310	8	1	800	834	-21	4	210	241
-14	5	573	565	19	7	411	378	6	11	364	332	9	1	704	721	-20	4	749	755
-11	5	1119	1075	-18	8	275	286	7	11	581	548	10	1	693	782	-17	4	554	555
-10	5	1362	1310	-17	8	536	554	8	11	611	595	12	1	839	825	-15	4	1235	1226
-9	5	262	262	-15	8	428	493	11	11	243	213	14	1	280	326	-14	4	901	903
-8	5	207	161	-14	8	422	459	13	11	240	190	15	1	331	330	-12	4	401	405
-6	5	868	842	-12	8	383	392	-10	12	530	550	16	1	398	396	-9	4	296	242
-5	5	340	389	-8	8	888	875	-9	12	252	280	17	1	705	751	-7	4	633	596
-4	5	868	838	-7	8	275	294	-5	12	332	389	20	1	286	278	-6	4	1261	1176
-2	5	940	904	-5	8	198	213	-4	12	541	565	22	1	365	307	-5	4	1242	1135
-1	5	2274	2176	-4	8	858	832	-3	12	316	347	23	1	570	557	-4	4	191	153
0	5	347	357	-3	8	421	387	-1	12	509	506	-23	2	311	280	-3	4	431	427
1	5	1440	1451	-1	8	219	202	0	12	327	306	-20	2	452	493	-2	4	871	871
2	5	592	614	1	8	426	460	1	12	294	333	-17	2	323	320	0	4	2092	2032
3	5	1402	1428	2	8	1225	1229	2	12	362	397	-15	2	487	508	1	4	741	713
4	5	1713	1735	6	8	640	626	4	12	737	739	-13	2	843	835	2	4	733	735
8	5	852	842	7	8	1179	1202	5	12	879	867	-12	2	203	175	3	4	1120	1174
9	5	349	346	9	8	268	218	-8	13	260	269	-11	2	459	458	4	4	317	330
11	5	258	271	10	8	462	496	-7	13	314	363	-10	2	224	223	5	4	811	841
12	5	709	735	11	8	286	336	-2	13	432	440	-9	2	226	225	6	4	301	308
13	5	585	583	12	8	324	366	-1	13	562	608	-7	2	171	164	7	4	872	861
14	5	464	465	13	8	250	237	1	13	593	546	-6	2	1336	1303	8	4	1029	1045
15	5	241	133	14	8	312	331	2	13	456	460	-5	2	1485	1420	9	4	233	248
17	5	421	437	15	8	522	492	5	13	289	288	-4	2	986	996	10	4	427	448
18	5	247	269	16	8	240	231	7	13	257	275	-3	2	522	512	12	4	195	158
19	5	639	635	17	8	275	218	**K = 5****				-2	2	758	708	13	4	539	570
21	5	211	202	-14	9	262	269	-23	0	237	274	-1	2	763	736	14	4	512	471
22	5	339	374	-13	9	231	304	-20	0	719	721	0	2	911	902	15	4	865	900
-22	6	278	281	-12	9	849	852	-19	0	248	206	1	2	469	475	17	4	452	444
-17	6	472	458	-11	9	593	587	-18	0	272	275	2	2	504	506	18	4	694	670
-16	6	261	197	-10	9	397	360	-17	0	265	241	3	2	1084	1193	19	4	239	192
-15	6	471	469	-9	9	307	290	-16	0	529	540	4	2	245	242	21	4	304	309
-13	6	1072	1040	-8	9	207	88	-15	0	265	264	5	2	856	919	22	4	204	205
-9	6	620	613	-7	9	229	232	-13	0	796	783	6	2	889	910	-18	5	753	745
-8	6	826	796	-6	9	388	406	-11	0	350	340	7	2	1355	1403	-17	5	726	756
-7	6	842	804	-2	9	277	296	-10	0	531	517	8	2	904	912	-16	5	241	174
-6	6	421	405	-1	9	278	306	-9	0	360	319	9	2	475	491	-13	5	404	372
-5	6	660	653	1	9	207	195	-8	0	392	364	10	2	838	905	-12	5	934	876
-4	6	254	206	2	9	838	815	-7	0	360	402	11	2	216	224	-10	5	364	380
-2	6	344	367	3	9	527	522	-6	0	1813	1829	13	2	379	392	-9	5	932	901
-1	6	714	687	4	9	890	508	-5	0	2028	2114	15	2	497	487	-7	5	193	223
0	6	875	852	5	9	692	682	-3	0	520	517	18	2	584	620	-6	5	463	489
1	6	1074	1070	6	9	433	441	-1	0	667	649	19	2	678	671	-5	5	468	487
2	6	992	987	7	9	221	235	1	0	607	649	20	2	758	782	-4	5	806	781
3	6	485	505	9	9	880	875	3	0	516	517	21	2	307	285	-3	5	1168	1094
5	6	226	260	10	9	412	447	5	0	2028	2114	-22	3	275	279	-2	5	724	683
6	6	693	665	11	9	435	456	6	0	1809	1829	-21	3	217	173	-1	5	351	340
7	6	812	871	12	9	595	621	7	0	358	402	-20	3	272	303	0	5	577	566
10	6	552	560	13	9	288	268	8	0	370	364	-19	3	510	487	1	5	403	385
11	6	357	368	-17	10	201	239	9	0	328	319	-18	3	412	474	2	5	715	748
12	6	270	213	-15	10	307	328	10	0	526	517	-17	3	1035	1026	3	5	499	520
13	6	231	252	-12	10	238	253	11	0	352	340	-15	3	478	455	4	5	180	189
14	6	222	225	-11	10	233	276	13	0	796	783	-13	3	236	223	5	5	595	622
15	6	337	270	-10	10	467	435	15	0	228	264	-12	3	422	447	6	5		

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K =	5**			0	8	1039	1006	-5	13	247	213	-10	2	718	695	5	4	686	713
7	5	342	336	4	8	668	694	-2	13	422	375	-9	2	373	315	6	4	248	263
9	5	610	633	5	8	832	823	-1	13	373	408	-7	2	716	702	7	4	318	369
11	5	779	792	7	8	539	515	0	13	356	351	-6	2	277	239	8	4	332	362
12	5	663	638	8	8	820	800	1	13	297	299	-5	2	217	203	9	4	345	364
14	5	663	686	9	8	306	277	2	13	334	322	-4	2	641	609	10	4	790	790
16	5	559	518	11	8	475	450	5	13	354	348	-3	2	1332	1319	11	4	398	424
17	5	395	402	13	8	650	638	**K =	6****			-2	2	813	770	13	4	826	847
18	5	380	351	14	8	318	330	-22	0	379	381	-1	2	665	646	14	4	536	526
20	5	656	662	18	8	449	397	-21	0	369	391	1	2	374	360	16	4	582	546
21	5	212	183	-16	9	362	393	-20	0	255	235	2	2	888	898	17	4	1006	971
-21	6	282	322	-15	9	369	384	-18	0	349	374	3	2	704	730	19	4	565	526
-19	6	258	227	-12	9	434	433	-15	0	369	354	4	2	934	948	-21	5	261	285
-16	6	296	336	-10	9	664	647	-14	0	727	736	5	2	976	1036	-19	5	275	255
-15	6	570	583	-8	9	639	603	-13	0	925	888	6	2	200	175	-16	5	741	742
-14	6	463	481	-7	9	261	298	-12	0	586	598	8	2	222	207	-15	5	428	410
-13	6	434	435	-5	9	580	577	-11	0	925	871	9	2	440	482	-14	5	760	802
-10	6	392	394	-4	9	845	837	-9	0	1142	1140	11	2	433	392	-11	5	1213	1145
-9	6	570	522	-3	9	481	413	-8	0	204	160	12	2	1009	1066	-10	5	355	345
-8	6	470	447	0	9	261	182	-7	0	1072	1103	13	2	992	1021	-9	5	352	365
-7	6	628	618	2	9	625	640	-6	0	370	369	14	2	260	217	-8	5	690	632
-6	6	683	677	3	9	672	675	-5	0	612	634	15	2	593	606	-6	5	222	223
-3	6	675	649	4	9	554	595	-4	0	693	651	16	2	514	538	-5	5	391	396
-2	6	221	241	5	9	404	417	-3	0	847	858	17	2	676	698	-4	5	958	927
-1	6	557	564	6	9	325	341	-1	0	704	684	18	2	297	300	-3	5	674	662
0	6	1253	1258	8	9	480	508	0	0	669	650	20	2	262	286	-2	5	662	631
1	6	446	422	9	9	499	487	1	0	671	684	22	2	283	273	-1	5	923	928
3	6	416	397	10	9	456	428	3	0	814	858	-22	3	332	335	1	5	285	289
4	6	446	428	11	9	681	701	4	0	685	651	-18	3	420	410	2	5	703	686
5	6	505	479	12	9	328	338	5	0	616	634	-16	3	818	823	3	5	770	809
6	6	476	444	16	9	337	312	6	0	360	369	-15	3	248	291	4	5	292	296
8	6	915	908	-16	10	241	293	7	0	1066	1103	-14	3	613	611	5	5	472	499
9	6	364	371	-13	10	434	480	8	0	217	160	-13	3	425	442	8	5	386	363
10	6	236	228	-12	10	426	433	9	0	1124	1140	-11	3	464	471	9	5	498	492
11	6	312	292	-11	10	431	432	11	0	878	871	-10	3	481	496	10	5	241	216
14	6	243	229	-10	10	337	351	12	0	605	598	-9	3	890	883	11	5	396	341
15	6	494	510	-8	10	344	392	13	0	888	888	-8	3	259	230	12	5	290	240
16	6	278	235	-7	10	377	390	14	0	722	736	-7	3	460	458	13	5	562	612
17	6	487	483	-5	10	580	584	15	0	396	354	-6	3	185	152	14	5	747	752
18	6	457	420	-2	10	899	882	18	0	351	374	-4	3	1258	1170	15	5	222	134
-20	7	270	260	-1	10	499	529	20	0	230	235	-3	3	176	158	16	5	1040	1035
-18	7	254	263	0	10	519	525	21	0	396	391	-2	3	246	260	17	5	344	279
-17	7	347	343	1	10	726	685	22	0	389	381	-1	3	1630	1539	19	5	212	204
-16	7	247	273	2	10	226	204	-22	1	349	345	0	3	978	942	20	5	254	224
-15	7	544	570	7	10	953	950	-19	1	225	213	1	3	391	352	-19	6	290	305
-12	7	559	526	8	10	506	508	-18	1	413	407	2	3	1507	1481	-17	0	277	297
-10	7	481	414	12	10	241	253	-14	1	959	963	3	3	218	222	-13	6	535	546
-8	7	286	279	13	10	481	485	-13	1	393	378	4	3	439	448	-11	6	423	426
-6	7	330	281	14	10	322	307	-12	1	814	809	5	3	502	530	-10	6	475	455
-5	7	675	692	-14	11	415	442	-11	1	896	879	6	3	470	515	-9	6	594	587
-4	7	1282	1278	-13	11	235	194	-9	1	520	524	7	3	362	350	-8	6	651	648
-3	7	501	477	-9	11	335	317	-8	1	189	135	9	3	339	353	-6	6	208	122
-1	7	230	233	-8	11	324	313	-7	1	679	671	11	3	283	284	-5	6	1225	1213
1	7	278	288	-7	11	256	245	-6	1	1150	1142	12	3	567	613	-4	6	393	406
2	7	832	853	-5	11	460	474	-5	1	281	271	13	3	835	860	-1	6	528	524
3	7	304	307	-4	11	523	518	-4	1	994	977	14	3	853	849	0	6	409	412
5	7	400	395	-2	11	470	452	-3	1	296	236	16	3	622	660	1	6	534	479
6	7	688	698	-1	11	341	326	-1	1	682	655	18	3	262	267	2	6	663	676
7	7	387	340	1	11	701	713	0	1	698	702	20	3	426	425	3	6	597	587
8	7	483	481	4	11	721	735	1	1	508	529	-21	4	335	346	4	6	305	354
9	7	537	507	5	11	321	292	2	1	991	1069	-20	4	233	210	5	6	513	544
11	7	717	710	6	11	283	294	3	1	352	384	-19	4	706	729	6	6	624	609
14	7	477	453	7	11	235	182	4	1	1467	1550	-18	4	247	219	8	6	641	635
17	7	220	171	9	11	491	520	5	1	316	329	-17	4	561	539	12	6	463	447
19	7	227	218	10	11	282	279	6	1	1924	1941	-16	4	277	215	13	6	719	733
-18	8	295	371	11	11	283	306	7	1	368	460	-12	4	405	365	14	6	340	373
-17	8	297	289	12	11	235	247	8	1	931	945	-11	4	624	602	15	6	424	391
-15	8	217	235	-11	12	285	288	9	1	440	444	-9	4	484	481	16	6	284	256
-14	8	531	506	-8	12	259	247	10	1	731	772	-8	4	483	515	17	6	446	436
-13	8	563	560	-5	12	461	499	11	1	524	556	-6	4	532	550	19	6	553	562
-12	8	314	349	-3	12	378	387	13	1	237	191	-4	4	343	340	-19	7	205	230
-11	8	267	221	-2	12	663	687	14	1	706	752	-3	4	882	840	-18	7	273	323
-10	8	335	317	-1	12	236	255	15	1	593	608	-2	4	592	550	-17	7	257	265
-7	8	1021	1026	1	12	397	435	18	1	660	623	-1	4	1617	1568	-16	7	255	258
-6	8	370	328	2	12	444	428	20	1	326	355	0	4	519	508	-14	7	596	592
-5	8	599	599	3	12	539	547	-22	2	356	318	1	4	517	508	-13	7	237	245
-4	8	567	538	6	12	232	215	-19	2	256	301	2	4	977	976	-9	7	253	253
-2	8	550	508	7	12	301	320	-15	2	755	767	3	4	259	260	-8	7	1188	1173
-1	8	368	300	-6	13	239	221	-12	2	515	512	4	4	253	296				

Table 31 (continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 6**																			
-7	7	584	570	0	11	452	455	-16	2	290	250	-19	5	333	345	-3	8	344	340
-6	7	1180	1170	2	11	406	399	-11	2	269	187	-14	5	608	637	-1	8	322	318
-5	7	256	73	3	11	225	218	-10	2	506	511	-12	5	257	277	0	8	431	414
-2	7	848	854	4	11	220	236	-9	2	646	623	-11	5	406	417	1	8	596	588
-1	7	612	635	6	11	439	417	-7	2	762	743	-10	5	438	431	5	8	945	952
0	7	417	402	7	11	391	382	-6	2	337	294	-9	5	414	408	6	8	267	283
1	7	340	366	8	11	289	321	-5	2	950	893	-8	5	783	745	7	8	293	175
2	7	272	295	9	11	270	209	-4	2	791	761	-6	5	714	679	9	8	404	424
3	7	496	527	10	11	315	323	-3	2	1707	1622	-5	5	826	834	10	8	511	459
4	7	418	409	11	11	219	224	-2	2	401	382	-2	5	480	459	11	8	501	514
5	7	401	422	-9	12	241	229	-1	2	811	802	-1	5	374	320	13	8	439	422
6	7	783	803	-7	12	390	380	1	2	584	627	0	5	794	798	-10	9	577	551
7	7	344	357	-5	12	373	334	2	2	476	506	1	5	249	197	-9	9	347	353
8	7	234	198	-4	12	320	341	3	2	364	365	2	5	376	387	-8	9	783	801
10	7	422	393	-3	12	611	640	4	2	425	475	3	5	277	278	-7	9	274	197
12	7	492	501	-2	12	252	200	5	2	183	166	4	5	223	190	-4	9	647	624
14	7	270	276	-1	12	580	584	6	2	527	520	5	5	326	307	-3	9	287	263
15	7	401	389	1	12	236	239	7	2	1174	1176	7	5	383	355	-2	9	764	748
16	7	554	554	4	12	502	471	8	2	209	207	8	5	258	251	1	9	430	381
-17	8	315	287	5	12	303	279	9	2	264	227	10	5	679	667	4	9	644	635
-13	8	249	268	7	12	234	234	10	2	726	750	14	5	530	567	8	9	472	459
-11	8	600	771	**K = 7****				11	2	337	347	15	5	327	310	10	9	414	366
-10	8	520	516	-21	0	482	534	12	2	302	280	16	5	376	398	11	9	359	350
-9	8	623	600	-17	0	585	592	13	2	508	521	18	5	796	779	12	9	580	577
-8	8	419	410	-15	0	632	683	14	2	373	398	19	5	203	145	13	9	272	273
-7	8	465	432	-14	0	284	303	15	2	1025	1050	-19	6	339	315	14	9	288	262
-6	8	747	719	-13	0	671	648	18	2	304	265	-17	6	416	402	-13	10	372	446
-5	8	853	811	-12	0	324	280	20	2	206	132	-16	6	354	353	-10	10	308	335
-3	8	827	815	-8	0	678	698	21	2	434	379	-15	6	583	560	-9	10	308	312
-2	8	211	62	-7	0	1481	1515	-20	3	476	523	-13	6	481	482	-7	10	346	353
-1	8	347	339	-6	0	256	250	-19	3	246	312	-10	6	228	228	-6	10	216	171
0	8	277	277	-5	0	933	930	-16	3	404	457	-9	6	620	579	-5	10	862	862
2	8	732	718	-4	0	447	452	-15	3	248	234	-8	6	223	138	-3	10	280	264
3	8	541	538	-3	0	378	399	-14	3	714	745	-7	6	822	820	-2	10	431	436
4	8	434	442	-2	0	509	477	-11	3	510	495	-5	6	285	272	1	10	594	603
7	8	457	445	-1	0	1538	1488	-8	3	484	500	-4	6	505	512	5	10	335	280
9	8	688	692	1	0	1455	1488	-7	3	603	567	-3	6	1013	982	7	10	333	351
10	8	340	327	2	0	505	477	-6	3	1281	1235	-2	6	554	548	8	10	251	258
11	8	835	834	3	0	403	399	-5	3	300	223	0	6	302	275	9	10	300	325
15	8	452	448	4	0	425	452	-4	3	962	939	2	6	204	198	11	10	285	285
16	8	412	382	5	0	940	930	-3	3	354	297	3	6	878	857	-8	11	201	210
-14	9	464	448	6	0	271	250	-2	3	374	338	5	6	860	882	-2	11	602	630
-12	9	222	242	7	0	1446	1515	0	3	864	846	6	6	235	241	4	11	397	401
-10	9	333	289	8	0	698	698	1	3	196	182	7	6	328	347	8	11	318	315
-9	9	342	354	12	0	286	280	2	3	305	288	11	6	674	694	9	11	207	233
-8	9	714	720	13	0	639	648	4	3	850	876	12	6	250	250	-5	12	628	677
-6	9	1279	1303	14	0	291	303	6	3	191	137	13	6	255	266	-4	12	400	420
-5	9	527	497	15	0	653	683	7	3	461	455	15	6	663	638	1	12	481	510
-4	9	570	562	17	0	597	592	9	3	293	346	17	6	443	458	3	12	204	152
-2	9	440	431	21	0	486	534	10	3	813	836	-16	7	719	704	**K = 8****			
0	9	327	364	-20	1	561	590	12	3	443	458	-14	7	483	482	-15	0	1050	1043
3	9	233	231	-19	1	332	257	13	3	246	212	-13	7	378	373	-14	0	260	217
4	9	287	350	-16	1	514	509	16	3	367	386	-12	7	329	353	-13	0	362	354
5	9	459	504	-14	1	577	543	18	3	526	544	-10	7	834	835	-9	0	990	987
6	9	750	732	-13	1	463	474	19	3	237	197	-9	7	240	182	-7	0	203	179
8	9	458	449	-12	1	508	486	-19	4	305	317	-8	7	704	677	-6	0	205	164
12	9	484	485	-10	1	508	898	-17	4	620	621	-7	7	675	701	-5	0	888	905
13	9	401	391	-8	1	672	606	-15	4	628	617	-6	7	747	757	-4	0	483	498
14	9	465	481	-7	1	546	593	-13	4	409	445	-4	7	783	751	-3	0	994	1019
-15	10	272	267	-6	1	725	776	-11	4	256	237	-3	7	316	316	-2	0	551	556
-11	10	252	281	-5	1	524	536	-9	4	716	663	-2	7	618	569	-1	0	851	796
-9	10	392	372	-4	1	1354	1339	-8	4	253	260	-1	7	227	206	1	0	775	796
-8	10	592	591	-2	1	948	942	-6	4	248	264	0	7	653	624	2	0	558	556
-7	10	737	720	-1	1	470	451	-3	4	1011	980	1	7	226	281	3	0	984	1019
-4	10	317	314	0	1	387	391	-2	4	690	645	2	7	393	385	4	0	488	498
-3	10	698	689	2	1	241	225	-1	4	275	287	3	7	324	274	5	0	913	905
0	10	290	334	3	1	214	190	0	4	466	473	4	7	247	251	7	0	213	179
1	10	222	83	4	1	1947	2023	1	4	324	339	8	7	971	978	9	0	954	987
2	10	291	270	5	1	882	952	2	4	318	322	10	7	216	165	13	0	370	354
3	10	656	681	7	1	366	402	3	4	586	585	12	7	309	281	14	0	274	217
4	10	283	295	8	1	416	468	4	4	285	321	13	7	420	390	15	0	1034	1043
5	10	500	542	9	1	696	744	5	4	319	30								

Table 31 (continued)

M	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
K = 8**				8	4	578	625	7	8	252	275	-14	2	297	365	11	5	285	322
5	1	282	232	9	4	683	676	8	8	229	219	-11	2	597	582	-15	6	324	347
6	1	821	837	10	4	312	377	9	8	448	463	-10	2	230	175	-14	6	269	288
7	1	364	411	11	4	275	306	11	8	282	283	-9	2	585	584	-13	6	459	469
8	1	653	647	13	4	735	748	12	8	374	350	-8	2	399	416	-12	6	283	268
10	1	457	505	14	4	320	355	13	8	455	432	-7	2	544	546	-11	6	376	408
12	1	826	864	15	4	396	410	-10	9	320	351	-6	2	384	375	-10	6	415	446
13	1	437	442	16	4	387	360	-9	9	298	327	-5	2	515	519	-9	6	442	423
14	1	392	380	17	4	240	242	-8	9	743	747	-4	2	255	238	-7	6	282	282
17	1	231	212	19	4	201	188	-7	9	295	285	-3	2	731	685	-6	6	255	227
18	1	302	293	-16	5	292	327	-6	9	396	404	0	2	632	658	-4	6	249	205
20	1	285	275	-14	5	493	496	-4	9	337	314	1	2	215	180	-3	6	749	720
-19	2	479	471	-12	5	259	289	-1	9	306	239	3	2	452	478	0	6	420	421
-18	2	396	378	-8	5	909	883	0	9	620	582	5	2	454	468	2	6	378	319
-17	2	480	495	-4	5	513	506	2	9	669	653	7	2	1019	1083	3	6	676	673
-16	2	365	342	-3	5	635	608	5	9	252	225	10	2	455	461	5	6	1185	1165
-15	2	731	736	-1	5	810	781	6	9	730	726	13	2	435	446	6	6	265	174
-11	2	305	324	0	5	219	197	9	9	257	271	15	2	396	373	7	6	384	359
-10	2	259	175	1	5	827	830	11	9	214	192	17	2	225	208	8	6	595	611
-9	2	740	708	2	5	1179	1196	-11	10	268	344	-17	3	432	448	11	6	677	685
-8	2	289	323	3	5	322	320	-10	10	207	228	-16	3	369	390	14	6	246	206
-7	2	552	532	4	5	491	465	-8	10	268	200	-14	3	549	573	15	6	287	323
-4	2	384	370	8	5	785	814	-7	10	639	646	-12	3	259	321	-14	7	203	201
-3	2	722	693	10	5	490	494	-5	10	411	395	-11	3	240	238	-12	7	278	305
-2	2	441	450	12	5	233	282	-3	10	416	460	-10	3	355	328	-10	7	466	423
-1	2	907	914	13	5	224	236	-1	10	303	368	-9	3	273	267	-6	7	718	719
3	2	475	497	15	5	217	235	1	10	336	345	-8	3	452	476	-5	7	310	337
4	2	284	304	16	5	703	687	3	10	519	496	-7	3	550	566	-4	7	220	172
5	2	1049	1111	17	5	252	301	9	10	405	417	-6	3	1265	1211	-1	7	312	285
7	2	223	261	18	5	315	252	-8	11	289	301	-5	3	446	388	0	7	295	341
9	2	771	815	-17	6	322	265	-4	11	458	498	-4	3	293	255	2	7	688	684
10	2	345	311	-13	6	660	660	-1	11	231	117	-3	3	839	800	3	7	467	482
12	2	385	402	-11	6	769	799	0	11	234	163	-2	3	530	515	4	7	537	471
13	2	625	653	-5	6	586	582	4	11	293	257	0	3	383	382	5	7	326	308
14	2	215	91	-4	6	578	582	6	11	720	706	1	3	266	270	6	7	477	459
15	2	356	362	-3	6	292	223	**K = 9****				2	3	670	669	8	7	645	660
17	2	269	271	-2	6	532	536	-17	0	740	753	4	3	826	838	11	7	391	377
-16	3	465	484	-1	6	617	605	-14	0	279	295	5	3	529	539	13	7	205	221
-15	3	345	390	0	6	274	236	-13	0	790	802	6	3	341	283	14	7	479	492
-14	3	757	739	2	6	286	315	-11	0	414	385	7	3	221	219	-13	8	605	663
-13	3	336	273	3	6	1059	1085	-10	0	406	363	10	3	513	508	-5	8	545	514
-12	3	609	567	5	6	962	968	-9	0	265	293	12	3	511	543	-3	8	671	675
-10	3	221	155	7	6	839	828	-7	0	958	951	13	3	312	289	-1	8	341	340
-9	3	271	245	9	6	441	453	-6	0	433	459	15	3	237	274	1	8	866	829
-8	3	654	648	10	6	278	303	-5	0	281	319	-14	4	379	396	5	8	729	747
-6	3	497	481	12	6	425	406	-3	0	656	663	-12	4	494	453	6	8	261	230
-5	3	295	304	13	6	767	775	-1	0	859	854	-11	4	546	544	8	8	384	413
-4	3	916	884	-16	7	378	410	1	0	796	854	-9	4	613	588	11	8	428	413
-3	3	325	347	-14	7	781	812	3	0	646	663	-8	4	269	279	-8	9	253	261
-2	3	292	299	-8	7	951	965	5	0	287	319	-6	4	699	703	-6	9	231	255
-1	3	568	512	-6	7	323	307	6	0	456	459	-4	4	424	444	-2	9	501	508
0	3	1035	1022	-5	7	387	400	7	0	932	951	-3	4	876	875	3	9	228	244
1	3	391	421	-4	7	326	378	8	0	209	107	-2	4	285	275	4	9	581	603
2	3	1029	1018	-2	7	607	579	10	0	375	363	-1	4	393	376	8	9	311	329
6	3	351	365	0	7	730	732	11	0	406	385	0	4	1160	1150	-5	10	422	417
8	3	473	512	2	7	541	520	13	0	790	802	1	4	333	370	-2	10	251	250
10	3	313	382	3	7	345	362	14	0	306	295	2	4	625	672	1	10	383	348
12	3	582	623	4	7	583	567	17	0	748	753	5	4	568	537	3	10	329	276
14	3	535	534	5	7	462	458	-17	1	373	401	7	4	981	996	5	10	318	331
16	3	412	399	6	7	1088	1064	-14	1	881	886	8	4	444	419	**K = 10****			
17	3	233	238	7	7	450	482	-12	1	308	312	11	4	396	394	-17	0	271	286
18	3	300	277	8	7	302	254	-10	1	309	323	14	4	261	224	-15	0	724	749
-19	4	296	274	9	7	362	372	-8	1	404	366	15	4	298	272	-14	0	462	455
-18	4	392	415	10	7	297	322	-7	1	464	456	17	4	233	216	-13	0	311	339
-17	4	620	629	14	7	344	358	-6	1	525	513	-17	5	404	396	-12	0	634	633
-16	4	279	292	15	7	303	333	-5	1	251	201	-16	5	328	358	-5	0	463	450
-15	4	229	291	16	7	762	737	-4	1	1314	1261	-14	5	601	577	-3	0	692	703
-12	4	216	137	-15	8	496	505	-3	1	378	365	-13	5	226	162	-2	0	341	334
-11	4	555	575	-14	8	225	174	-2	1	487	426	-12	5	515	527	2	0	305	334
-9	4	482	467	-12	8	266	290	0	1	490	516	-9	5	299	272	3	0	664	703
-6	4	262	215	-11	8	712	708	2	1	418	483	-6	5	755	721	5	0	445	450
-5	4	277	231	-8	8	350	353	3	1	312	351	-4	5	235	169	9	0	228	231
-4	4	278	283	-7	8	364	393	4	1	1248	1297	-3	5	541	522	12	0	644	633
-2	4	473	518	-6	8	465	471	7	1	437	425	0	5	462	480	13	0	363	339
-1	4	552	508	-5	8	867	843	10	1	632	631	2	5	575	560	14	0	449	455
0	4	516	538	-3	8	720	714	14	1	406	373	3	5	443	456	15	0	714	749
1	4	688	690	-2	8	257	249	16	1	341	338	4	5	388	373	17	0	280	286
2	4	622	667	0	8	291	238	17	1	319	277	5	5	761	762	-16	1	425	434
3	4	624	658	2	8	457	448	18	1	477	453	6	5	840	850	-15	1	333	354
4	4	359	307	3	8	1355	1304	-19	2	200	251	8	5	615	615	-12	1	539	554
5	4	887	891	4	8	286	319	-17	2	687	716	10	5	450	469	-11	1	402	417
6	4	691	705	5	8	361	391	-15	2										

TABLE 32: ATOM COORDINATES
AND ISOTROPIC TEMPERATURE FACTORS

ATOM	x	y	z	B
Nb	0.58136(2)	0.21418(5)	0.19528(4)	2.47*
As	0.20939(3)	0.15780(7)	0.26735(6)	3.31*
S1	0.52186(8)	0.1130(1)	0.0746(1)	3.26*
S2	0.57210(8)	0.3413(2)	0.0567(1)	3.60*
S3	0.51630(8)	0.1329(2)	0.3169(1)	3.75*
S4	0.56193(8)	0.3659(1)	0.3010(1)	3.54*
S5	0.63390(8)	0.0503(1)	0.2242(1)	3.54*
S6	0.68163(7)	0.2798(2)	0.1989(1)	3.51*
C11	0.4876(3)	0.2027(6)	-0.0067(5)	2.82*
C12	0.4412(3)	0.1741(6)	-0.0731(5)	3.43*
C13	0.4164(3)	0.2420(7)	-0.1411(6)	4.21*
C14	0.4364(3)	0.3455(7)	-0.1445(6)	4.09*
C15	0.4824(3)	0.3765(6)	-0.0820(6)	3.69*
C16	0.5091(3)	0.3074(6)	-0.0132(5)	3.06*
C21	0.5210(3)	0.2120(7)	0.4254(5)	3.81*
C22	0.4989(4)	0.1770(7)	0.5182(7)	4.93*
C23	0.4971(4)	0.2458(9)	0.6005(7)	6.19*
C24	0.5165(4)	0.3452(9)	0.5921(7)	6.09*
C25	0.5395(3)	0.3818(7)	0.5039(7)	4.70*
C26	0.5405(3)	0.3143(6)	0.4180(6)	3.41*
C36	0.7256(3)	0.1716(6)	0.1733(5)	3.19*

Table 32 (continued)

ATOM	x	y	z	B
C35	0.7837(3)	0.1875(6)	0.1505(6)	3.86*
C34	0.8198(3)	0.1032(8)	0.1328(6)	4.97*
C33	0.7983(4)	0.0024(7)	0.1415(6)	5.04*
C32	0.7418(4)	-0.0137(6)	0.1648(6)	4.66*
C31	0.7040(3)	0.0717(6)	0.1835(5)	3.17*

RIGID BODIES

(a) Phenyl Carbon Atoms

C41	0.1589(2)	0.0435(3)	0.2397(4)	3.4(2)
C42	0.1656(3)	-0.0184(4)	0.1533(3)	4.1(2)
C43	0.1319(3)	-0.1087(4)	0.1387(4)	4.5(2)
C44	0.0915(2)	-0.1371(3)	0.2105(4)	4.7(2)
C45	0.0847(3)	-0.0752(4)	0.2968(3)	4.9(2)
C46	0.1184(3)	0.0151(4)	0.3114(4)	4.3(2)
D	3.710(3) ^a			
E	0.982(4)			
F	4.924(4)			
C51	0.1688(2)	0.2697(3)	0.3259(4)	3.4(2)
C52	0.1118(2)	0.2914(4)	0.2916(4)	4.4(2)
C53	0.0845(1)	0.3833(4)	0.3226(3)	4.9(2)
C54	0.1140(2)	0.4533(3)	0.3877(4)	4.9(2)
C55	0.1710(2)	0.4315(4)	0.4220(4)	4.7(2)
C56	0.1984(1)	0.3397(4)	0.3910(3)	4.0(2)

Table 32 (continued)

ATOM	x	y	z	B
D	5.779 (3)			
E	2.731 (4)			
F	4.418 (3)			
C61	0.2679 (4)	0.1098 (4)	0.3600 (10)	3.6 (2)
C62	0.3211 (5)	0.0725 (4)	0.3265 (5)	5.1 (2)
C63	0.3613 (3)	0.0279 (4)	0.3961 (7)	5.7 (2)
C64	0.3482 (4)	0.0207 (4)	0.4990 (10)	5.1 (2)
C65	0.2950 (5)	0.0580 (4)	0.5318 (5)	4.9 (2)
C66	0.2548 (3)	0.1026 (4)	0.4622 (7)	4.3 (2)
D	2.023 (3)			
E	1.217 (8)			
F	5.084 (8)			
C71	0.2370 (5)	0.2098 (4)	0.1429 (8)	3.3 (1)
C72	0.1963 (5)	0.2212 (4)	0.0622 (4)	4.4 (2)
C73	0.2126 (7)	0.2680 (5)	-0.0285 (7)	5.5 (2)
C74	0.2696 (5)	0.3034 (4)	-0.0384 (8)	5.4 (2)
C75	0.3103 (5)	0.2920 (4)	0.0423 (4)	6.3 (2)
C76	0.2940 (7)	0.2452 (5)	0.1330 (7)	5.2 (2)
D	1.109 (4)			
E	2.521 (8)			
F	4.425 (8)			

Table 32 (continued)

ATOM	x	y	z	B
(b) Phenyl Hydrogen Atoms				
H1	0.7990	0.2619	0.1446	4.5
H2	0.8613	0.1152	0.1151	5.0
H3	0.8243	-0.0598	0.1281	5.0
H4	0.7250	-0.0880	0.1705	4.5
D	3.159			
E	0.277			
F	5.085			
H5	0.4840	0.1029	0.5229	5.4
H6	0.4809	0.2184	0.6663	6.0
H7	0.5158	0.3948	0.6530	6.0
H8	0.5537	0.4557	0.4962	5.4
D	3.448			
E	1.285			
F	1.748			
H9	0.4267	0.0982	-0.0685	4.1
H10	0.3826	0.2199	-0.1869	4.7
H11	0.4182	0.3963	-0.1949	4.7
H12	0.4978	0.4509	-0.0846	4.1
D	0.281			
E	2.406			
F	4.929			
H13	0.1945	0.0016	0.1020	4.6

Table 32 (continued)

ATOM	x	y	z	B
H14	0.1369	-0.1535	0.0773	5.1
H15	0.0674	-0.2020	0.2004	5.0
H16	0.0556	-0.0953	0.3482	5.5
H17	0.1132	0.0597	0.3730	5.1
D	3.707			
E	0.981			
F	5.973			
H18	0.0905	0.2414	0.2452	5.0
H19	0.0436	0.3989	0.2983	5.9
H20	0.0944	0.5191	0.4100	5.5
H21	0.1922	0.4816	0.4685	5.1
H22	0.2391	0.3241	0.4154	4.7
D	5.779			
E	2.732			
F	5.465			
H23	0.3305	0.0773	0.2529	5.1
H24	0.3994	0.0013	0.3725	6.1
H25	0.3770	-0.0107	0.5486	5.8
H26	0.2856	0.0531	0.6052	5.3
H27	0.2166	0.1290	0.4856	4.7
D	2.020			
E	1.219			
F	6.134			

Table 32 (continued)

ATOM	x	y	z	B
H28	0.1555	0.1957	0.0691	5.1
H29	0.1836	0.2756	-0.0864	5.6
H30	0.2814	0.3364	-0.1034	6.2
H31	0.3511	0.3173	0.0352	6.8
H32	0.3230	0.2374	0.1909	5.6
D	1.111			
E	2.515			
F	5.467			

*These values are equivalent isotropic temperature factors⁸¹ corresponding to the anisotropic thermal parameters shown in Table 33.

^aD, E, and F are the angles by which the coordinates of the rigid body are rotated with respect to a set of axes X, Y, Z. The origin of these axes is placed at the centre of the ring with the X axis parallel to a^* , the Z axis parallel to c , and the Y axis parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c .

TABLE 33: ANISOTROPIC THERMAL PARAMETERS (\AA^2)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	0.0324(3)	0.0310(4)	0.0302(3)	-0.0003(3)	0.0007(2)	-0.0025(3)
As	0.0385(5)	0.0502(6)	0.0370(5)	-0.0037(4)	0.0025(4)	-0.0057(5)
S1	0.0510(12)	0.0340(11)	0.0383(11)	-0.0004(9)	-0.0071(9)	-0.0022(9)
S2	0.0515(12)	0.0430(12)	0.0420(11)	-0.0098(11)	-0.0024(9)	0.0051(10)
S3	0.0547(12)	0.0407(13)	0.0475(12)	-0.0054(10)	0.0120(10)	-0.0034(10)
S4	0.0413(11)	0.0397(12)	0.0535(12)	-0.0008(9)	0.0059(9)	-0.0093(10)
S5	0.0457(12)	0.0388(12)	0.0496(13)	0.0048(9)	-0.0042(10)	0.0083(10)
S6	0.0385(10)	0.0394(12)	0.0556(12)	-0.0022(10)	0.0009(9)	-0.0093(11)
Cl1	0.036(4)	0.036(5)	0.036(4)	-0.005(4)	-0.000(3)	-0.001(4)
Cl2	0.045(5)	0.048(5)	0.037(4)	-0.007(4)	-0.006(4)	0.000(4)
Cl3	0.049(5)	0.069(7)	0.041(5)	0.004(5)	-0.004(4)	0.004(5)
Cl4	0.054(5)	0.062(6)	0.039(5)	0.011(5)	-0.007(4)	0.008(5)
Cl5	0.053(5)	0.041(5)	0.046(5)	0.006(4)	0.002(4)	0.006(4)
Cl6	0.036(4)	0.049(5)	0.031(4)	0.006(4)	0.005(3)	-0.005(4)
C21	0.040(4)	0.066(6)	0.039(5)	0.006(5)	0.007(4)	-0.008(5)

Table 33 (continued)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C22	0.063(6)	0.067(7)	0.058(6)	0.008(5)	0.011(5)	0.010(5)
C23	0.079(7)	0.111(9)	0.045(6)	0.022(7)	0.011(5)	0.005(6)
C24	0.081(7)	0.109(9)	0.041(6)	0.032(7)	-0.006(5)	-0.021(6)
C25	0.045(5)	0.076(7)	0.057(6)	0.014(5)	-0.011(4)	-0.025(5)
C26	0.040(4)	0.044(5)	0.046(5)	0.006(4)	0.000(4)	-0.007(4)
C31	0.038(4)	0.048(5)	0.034(4)	0.010(4)	-0.002(4)	0.001(4)
C32	0.061(6)	0.053(6)	0.063(6)	0.010(5)	-0.004(5)	0.011(5)
C33	0.061(6)	0.067(7)	0.064(6)	0.029(5)	0.010(5)	0.012(5)
C34	0.043(5)	0.086(7)	0.061(6)	0.020(5)	0.005(4)	0.019(6)
C35	0.040(5)	0.066(6)	0.040(5)	0.003(4)	-0.004(4)	0.007(4)
C36	0.045(5)	0.042(5)	0.034(4)	0.007(4)	-0.002(4)	0.002(4)

TABLE 34: INTRA-IONIC CONTACTS (\AA)

ATOMS	DISTANCE	ATOMS	DISTANCE
Nb-S1	2.428 (2)	S2-S6	3.178 (3)
Nb-S2	2.442 (2)	S4-S6	3.294 (3)
Nb-S3	2.458 (2)	S1-C11	1.736 (7)
Nb-S4	2.433 (2)	S2-C16	1.740 (7)
Nb-S5	2.436 (2)	S3-C21	1.747 (7)
Nb-S6	2.451 (2)	S4-C26	1.760 (8)
As-C41	1.891 (4)	S5-C31	1.739 (7)
As-C51	1.883 (4)	S6-C36	1.750 (7)
As-C61	1.880 (4)	C11-C12	1.402 (9)
As-C71	1.896 (4)	C12-C13	1.356 (10)
S1-S2	3.143 (3)	C13-C14	1.398 (10)
S3-S4	3.160 (3)	C14-C15	1.374 (10)
S5-S6	3.147 (3)	C15-C16	1.392 (9)
S1-S3	3.204 (3)	C16-C11	1.424 (9)
S1-S5	3.282 (3)	C21-C22	1.410 (10)
S3-S5	3.184 (3)	C22-C23	1.396 (12)
S2-S4	3.245 (3)	C23-C24	1.349 (13)
C24-C25	1.374 (12)	C33-C34	1.383 (12)
C25-C26	1.422 (10)	C34-C35	1.382 (11)
C26-C21	1.385 (10)	C35-C36	1.395 (9)
C31-C32	1.419 (10)	C36-C31	1.375 (10)
C32-C33	1.363 (11)		

TABLE 35: INTRA-IONIC ANGLES (DEGREES)

ATOMS	ANGLES	ATOMS	ANGLES
S1-Nb-S2	80.40 (7)	Nb-S3-C21	105.5 (3)
S3-Nb-S4	80.47 (7)	Nb-S4-C26	105.4 (3)
S5-Nb-S6	80.18 (7)	Nb-S5-C31	106.1 (3)
S1-Nb-S5	84.87 (7)	Nb-S6-C36	106.0 (3)
S1-Nb-S3	81.94 (7)	S1-C11-C16	120.2 (6)
S3-Nb-S5	81.18 (7)	S2-C16-C11	119.0 (5)
S2-Nb-S4	83.46 (7)	S3-C21-C26	119.7 (6)
S2-Nb-S6	81.03 (7)	S4-C26-C21	121.1 (6)
S4-Nb-S6	84.81 (7)	S5-C31-C36	121.1 (6)
S1-Nb-S4	133.25 (7)	S6-C36-C31	119.9 (6)
S1-Nb-S6	134.51 (7)	C41-As-C51	110.6 (2)
S3-Nb-S2	136.61 (7)	C41-As-C61	107.1 (2)
S3-Nb-S6	136.50 (7)	C41-As-C71	109.0 (2)
S5-Nb-S2	135.63 (7)	C51-As-C61	109.6 (2)
S5-Nb-S4	133.86 (7)	C51-As-C71	105.9 (2)
Nb-S1-C11	106.5 (2)	C61-As-C71	114.6 (2)
Nb-S2-C16	106.1 (3)	C11-C12-C13	122.4 (7)
C12-C13-C14	119.5 (7)	C25-C26-C21	120.0 (8)
C13-C14-C15	120.0 (7)	C26-C21-C22	119.1 (8)
C14-C15-C16	121.2 (7)	C31-C32-C33	121.1 (8)
C15-C16-C11	120.0 (7)	C32-C33-C34	120.3 (8)
C16-C11-C12	117.8 (6)	C33-C34-C35	119.5 (8)

Table 35 (continued)

ATOMS	ANGLES	ATOMS	ANGLES
C21-C22-C23	119.6 (8)	C34-C35-C36	120.4 (8)
C22-C23-C24	120.5 (9)	C35-C36-C31	120.5 (7)
C23-C24-C25	121.8 (10)	C36-C31-C32	118.0 (7)
C24-C25-C26	119.9 (9)	S3-S1-S5	58.80 (6)
S6-S2-S4	61.69 (6)	S5-S3-S1	61.83 (6)
S2-S4-S6	58.16 (6)	S3-S5-S1	59.37 (6)
S2-S6-S4	60.15 (6)		

TABLE 36: INTER-IONIC CONTACTS (\AA)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
S1	H9	$\bar{x}+1, \bar{y}, \bar{z}$	2.942
S1	H20	$1/2-x, 1/2+y-1, 1/2-z$	2.942
S1	C54	$1/2+x, 1/2-y, 1/2+z-1$	3.409 (6)
S1	S1	$\bar{x}+1, \bar{y}, \bar{z}$	3.607 (4)
S1	C53	$1/2+x, 1/2-y, 1/2+z-1$	3.661 (6)
S2	H17	$1/2+x, 1/2-y, 1/2+z-1$	2.913
S3	H15	$1/2-x, 1/2+y, 1/2-z$	2.855
S4	H3	$1/2-x+1, 1/2+y, 1/2-z$	2.901
S4	C44	$1/2-x, 1/2+y, 1/2-z$	3.523 (5)
S4	C45	$1/2-x, 1/2+y, 1/2-z$	3.640 (5)
S5	H25	$\bar{x}+1, y, \bar{z}+1$	3.048
S6	H29	$1/2+x, 1/2-y, 1/2+z$	2.908
S6	C33	$1/2-x+1, 1/2+y, 1/2-z$	3.549 (9)
S6	C32	$1/2-x+1, 1/2+y, 1/2-z$	3.606 (8)
S6	C73	$1/2+x, 1/2-y, 1/2+z$	3.680 (5)
C35	C65	$1/2+x, 1/2-y, 1/2+z-1$	3.612 (10)
C35	C66	$1/2+x, 1/2-y, 1/2+z-1$	3.688 (9)
C34	H14	$\bar{x}+1, \bar{y}, \bar{z}$	3.038
C32	H21	$1/2+x, 1/2-y, 1/2+z-1$	2.811
C32	C55	$1/2+x, 1/2-y, 1/2+z-1$	3.682 (9)
C31	H21	$1/2+x, 1/2-y, 1/2+z-1$	2.909
C31	C55	$1/2+x, 1/2-y, 1/2+z-1$	3.495 (8)

Table 36 (continued)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
C21	C44	$1/2-x, 1/2+y, 1/2-z$	3.638(9)
C23	H18	$1/2+x, 1/2-y, 1/2+z$	2.821
C23	C52	$1/2+x, 1/2-y, 1/2+z$	3.606(11)
C25	H28	$1/2+x, 1/2-y, 1/2+z$	2.942
C25	H8	$\bar{x}+1, \bar{y}+1, \bar{z}+1$	2.980
C25	C25	$\bar{x}+1, \bar{y}+1, \bar{z}+1$	3.517(17)
C26	H15	$1/2-x, 1/2+y, 1/2-z$	2.886
C26	C44	$1/2-x, 1/2+y, 1/2-z$	3.472(8)
C11	C53	$1/2+x, 1/2-y, 1/2+z-1$	3.400(9)
C12	H20	$1/2-x, 1/2+y-1, 1/2-z$	3.049
C12	C53	$1/2+x, 1/2-y, 1/2+z-1$	3.685(9)
C13	H6	$x, y, z-1$	2.996
C13	C75	x, y, z	3.549(10)
C13	H31	x, y, z	2.966
C16	H16	$1/2-x, 1/2+y, 1/2-z$	2.947
C42	C56	$1/2-x, 1/2+y-1, 1/2-z$	3.676(7)
C44	H32	$1/2-x, 1/2+y-1, 1/2-z$	2.811
C44	C76	$1/2-x, 1/2+y-1, 1/2-z$	3.609(7)
C45	H31	$1/2-x, 1/2+y-1, 1/2-z$	2.947
C45	H12	$1/2+x-1, 1/2-y, 1/2+z$	3.023
C45	C75	$1/2-x, 1/2+y-1, 1/2-z$	3.577(8)
C45	C76	$1/2-x, 1/2+y-1, 1/2-z$	3.699(7)
C53	C63	$1/2-x, 1/2+y, 1/2-z$	3.672(7)

Table 36 (continued)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE
C54	H23	$1/2-x, 1/2+y, 1/2-z$	2.778
C54	C62	$1/2-x, 1/2+y, 1/2-z$	3.574 (7)
C55	H23	$1/2-x, 1/2+y, 1/2-z$	2.956
C64	C73	$1/2-x, 1/2+y-1, 1/2-z$	3.537 (8)
C65	H1	$1/2+x-1, 1/2-y, 1/2+z$	2.731
C65	C74	$1/2-x, 1/2+y-1, 1/2-z$	3.571 (8)
C66	H1	$1/2+x-1, 1/2-y, 1/2+z$	3.095
H9	H20	$1/2-x, 1/2+y-1, 1/2-z$	2.380

TABLE 37: LEAST SQUARES PLANE CALCULATIONS

(A) ATOMS FORMING PLANE: Nb, S1, S2

$$\begin{aligned} \text{EQUATION OF PLANE: } & -0.8413X + 0.3686Y + 0.3953Z \\ & + 9.1444 = 0.0^a \end{aligned}$$

(B) ATOMS FORMING PLANE: Nb, S3, S4

$$\begin{aligned} \text{EQUATION OF PLANE: } & 0.7683X - 0.2315Y + 0.5967Z \\ & - 11.0967 = 0.0 \end{aligned}$$

(C) ATOMS FORMING PLANE: Nb, S5, S6

$$\begin{aligned} \text{EQUATION OF PLANE: } & -0.0706X + 0.1393Y + 0.9877Z \\ & - 1.9792 = 0.0 \end{aligned}$$

(D) ATOMS FORMING PLANE: S1, S2, C11, C12, C13, C14
C15, C16

$$\begin{aligned} \text{EQUATION OF PLANE: } & -0.6239X + 0.3044Y + 0.7198Z \\ & + 6.3172 = 0.0 \end{aligned}$$

DISTANCES OF ATOMS FROM PLANE (\AA):

S1	-0.001(2)	S2	0.009(2)
C11	-0.048(7)	C12	0.041(7)
C13	0.078(8)	C14	0.010(8)
C15	-0.071(8)	C16	-0.086(7)
Nb	-0.7144(6)		

(E) ATOMS FORMING PLANE: S3, S4, C21, C22, C23, C24,
C25, C26

Table 37 (continued)

EQUATION OF PLANE: $0.9191X - 0.3096Y + 0.2438Z$

$$- 11.2653 = 0.0$$

DISTANCES OF ATOMS FROM PLANE (\AA):

S3	0.004 (2)	S4	0.004 (2)
C21	-0.090 (7)	C22	-0.012 (9)
C23	-0.067 (9)	C24	0.060 (9)
C25	-0.023 (8)	C26	-0.067 (7)
Nb	-0.7099 (6)		

(F) ATOMS FORMING PLANE: S5, S6, C31, C32, C33, C34,
C35, C36.

EQUATION OF PLANE: $0.2788X + 0.0011Y + 0.9603Z$

$$- 6.8577 = 0.0$$

DISTANCES OF ATOMS FROM PLANE (\AA):

S5	-0.006 (2)	S6	0.001 (2)
C31	0.036 (7)	C32	-0.042 (8)
C33	-0.052 (9)	C34	-0.004 (9)
C35	0.057 (8)	C36	0.055 (7)
Nb	0.6869 (6)		

(G) ATOMS FORMING PLANE: S1, S3, S5

EQUATION OF PLANE: $-0.3396X - 0.9393Y + 0.0484Z$

$$+ 5.3688 = 0.0$$

DISTANCES OF ATOMS FROM PLANE (\AA):

Nb	1.5787 (6)
----	------------

(H) ATOMS FORMING PLANE: S2, S4, S6

Table 37 (continued)

EQUATION OF PLANE: $-0.3423X - 0.9380Y + 0.0545Z$
 $+ 8.5348 = 0.0$
 DISTANCES OF ATOMS FROM PLANE (\AA):
 Nb $-1.5699(6)$

$^a x$, y and z are in \AA and refer to the orthogonal coordinates along a , b , c^* .

TABLE 38: DIHEDRAL ANGLES BETWEEN SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE
Nb, S1, S2	Nb, S3, S4	119.7°
Nb, S1, S2	Nb, S5, S6	120.1°
Nb, S3, S4	Nb, S5, S6	120.2°
Nb, S1, S2	S1, S2, C11, C12, C13, C14, C15, C16	22.8°
Nb, S3, S4	S3, S4, C21, C22, C23, C24, C25, C26	22.6°
Nb, S5, S6	S5, S6, C31, C32, C33, C34, C35, C36	21.8°
S1, S3, S5	S2, S4, S6	0.6°

DESCRIPTION OF STRUCTURE

The portion of the molecule of major interest, i.e. the $\text{Nb}(\text{bdt})_3^-$ anion, is shown in the three dimensional representation in Fig. 14. The metal is surrounded approximately equidistantly by six sulfur atoms in the form of a trigonal prism, thus it has approximate C_{3h} symmetry. The dithiolene ligands radiate from the metal in a "paddle-wheel" arrangement as was the case for $\text{Mo}(\text{bdt})_3$ and the other trigonal prismatic dithiolenes.^{129,130,132} The prism is not however as regular as that in $\text{Mo}(\text{bdt})_3$, with a significant range in niobium-sulfur distances from $2.428(2) \text{ \AA}$ to $2.458(2) \text{ \AA}$. The mean Nb-S distance (2.441 \AA) is also significantly longer than the Mo-S distance (2.367 \AA) in $\text{Mo}(\text{bdt})_3$ and thus is the longest metal-sulfur distance observed in any of the trigonal prismatic molecules (Table 48).

It is interesting that in the previous trigonal prismatic structures the metal-sulfur bond lengths had been amazingly constant, considering that the covalent and ionic radii¹³³ of vanadium differed, by approximately 0.07 \AA , from those of molybdenum and rhenium. $\text{Nb}(\text{bdt})_3^-$ is therefore the first example of a prism in which this is no longer true; the Nb-S distance being approximately 0.11 \AA longer than

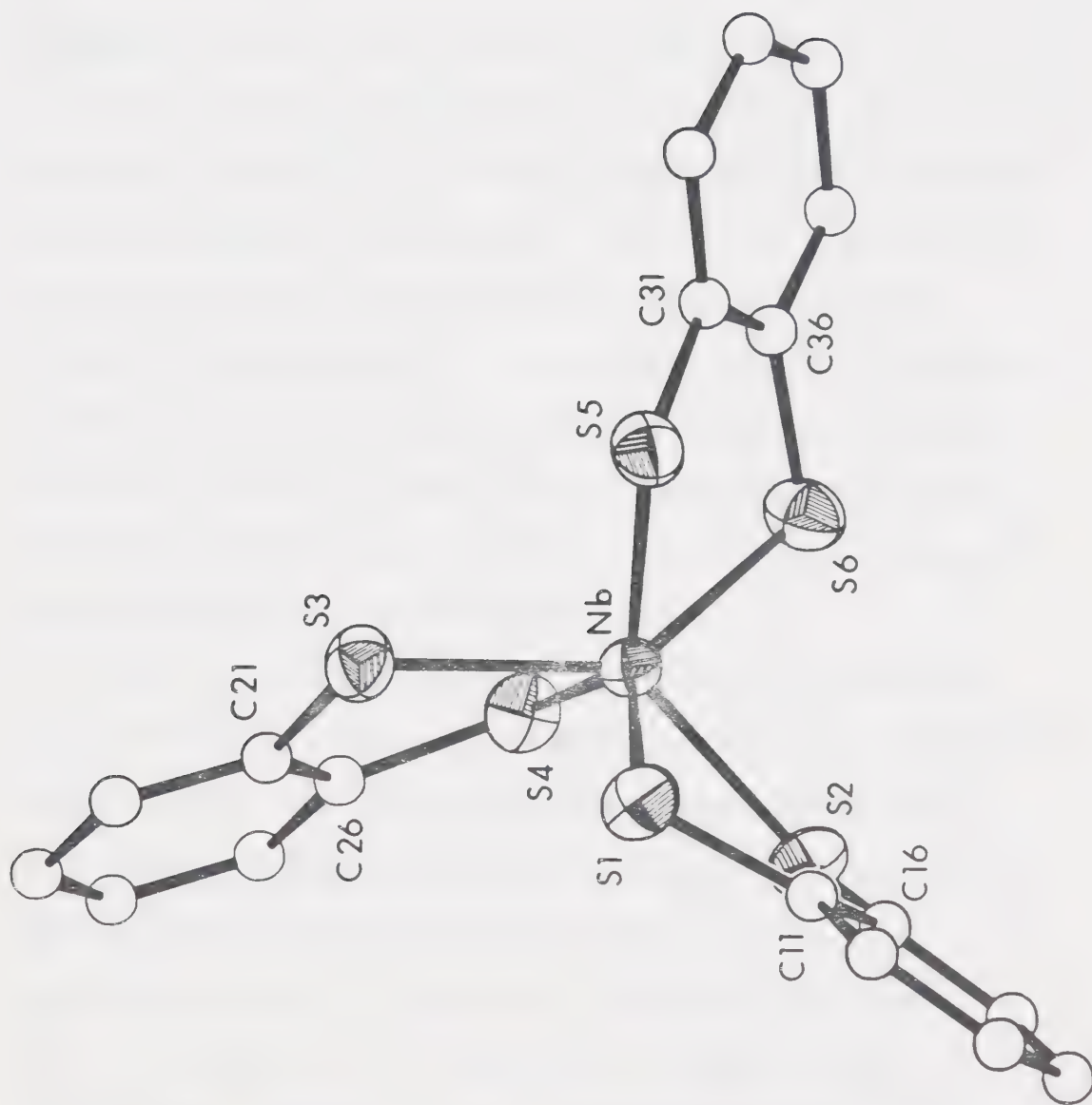


Fig. 14: A PERSPECTIVE VIEW OF THE $\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3^-$ ANION.

the metal-sulfur distances in the three other prisms and also 0.074 \AA longer than in $\text{Mo}(\text{bdt})_3$ (to which this comparison is most useful). The increase in metal-sulfur distances progressing from the molybdenum to the niobium complex is approximately consistent with the corresponding increase in the metal covalent radii.¹³³ Although the values for the metal covalent radii are ambiguous (especially for $\text{Nb}(\text{bdt})_3^-$ since the extra electron will expand the niobium orbitals increasing its radius from that of the neutral species), a very rough comparison is obtained using Pauling's values. This yields a predicted increase in metal-sulfur bonds of about 0.05 \AA when calculated using the neutral atom radii.

The constancies of the metal-sulfur distances in the previous trigonal prisms, in spite of differing metal radii, had been attributed as a consequence of proposed interligand S-S bonding.¹²⁴ Thus the difference in Nb-S distances compared with Mo-S distances tends to indicate a possible breakdown in S-S bonding and an expected increase in S-S distances. Because of the relatively fixed ligand bite this should manifest itself in longer interligand S-S distances compared to intraligand S-S distances. This is in fact what is observed with the

mean interligand S-S distance (3.231 \AA) being significantly longer than the intraligand S-S distance (3.150 \AA). Here again slight distortions are obvious with a range in interligand S-S distances from $3.178(3) \text{ \AA}$ to $3.294(3) \text{ \AA}$.

The sulfur-carbon distances (1.745 \AA), although similar to the other *tris* dithiolenes, are longer than any observed previously and more significantly are longer than those in $\text{Mo}(\text{bdt})_3$ (1.727 \AA) where the same ligand is involved. Thus the sulfur-carbon bonds have less double bond character in the niobium complex and the ligands are therefore more dithiolate and less dithioketonic in character than for $\text{Mo}(\text{bdt})_3$. The mean carbon-carbon distance within the ligands is again consistent with those observed in benzene¹⁵⁸ and in several disubstituted benzene derivatives,¹⁵⁹ as mentioned in Chapter VI. Again, as was the case for $\text{Mo}(\text{bdt})_3$, there is a wide range in C-C distances (Fig. 15). From the diagram showing the average C-C bond lengths one sees that the C2-C3, C3-C4, and C4-C5 distances are significantly shorter than the other three. This may be interpreted as indicating some contribution from the dithioketonic formulation but this simple interpretation should not be made in the absence of a full analysis of the thermal

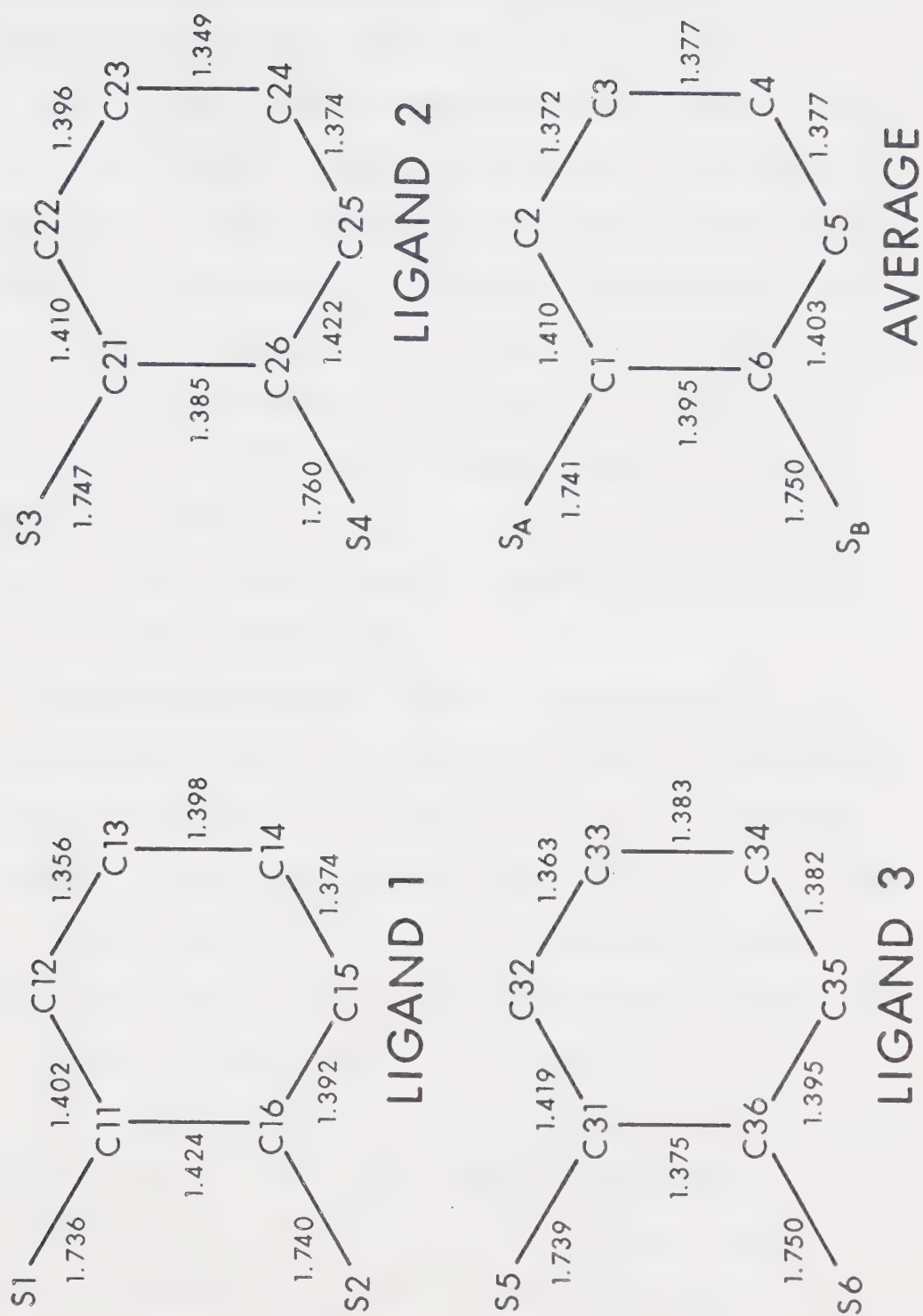


Fig. 15: DIMENSIONS WITHIN THE DITHIOLENE LIGANDS.

parameters and an assessment of their effect on the observed uncorrected bond distances.

The intra- and interligand S-Nb-S angles average 80.35° and 82.88° respectively and are therefore an indication of the slight distortion from trigonal prismatic coordination. Possibly a more significant indication of the distortion, however, is the *range* in the interligand S-Nb-S angles, from $84.87(7)^\circ$ to $81.03(7)^\circ$. The S-Nb-S angles, involving sulfur atoms approximately *trans* to each other, average 135.06° and is again similar to the value of $136(1)^\circ$ found in the other prisms.

The two triangular faces of the prism deviate slightly from being parallel, the angle between their normals being 0.6° . In addition the angles between the NbS₂ planes, as shown in Table 38, are all close to the expected 120° . The Nb-S-C angles average 105.9° and are all in close agreement with each other.

The S-C-C angles ($S_A-C_1-C_6$ and $S_B-C_6-C_1$ in Fig. 15) average 120.1° and are close to the expected value of 120° . This good internal agreement of the Nb-S-C and S-C-C angles adds further proof that the deviations in the interligand S-Nb-S angles are indeed significant.

As was observed in Mo(bdt)₃, Mo(S₂C₂H₂)₃,¹³⁰

and $\text{Mo}[\text{Se}_2\text{C}_2(\text{CF}_3)_2]_3$,¹⁵² the ligand planes again deviate considerably from the corresponding MS_2 planes. These deviations are more regular in $\text{Nb}(\text{bdt})_3^-$ than in $\text{Mo}(\text{bdt})_3$ (see Table 49). Their mean values, 22.4° and 21.4° , respectively are however in good agreement and both are larger than the values of 18° and 18.6° observed in $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ and $\text{Mo}[\text{Se}_2\text{C}_2(\text{CF}_3)_2]_3$ respectively. That these dihedral angles are irregular in $\text{Mo}(\text{bdt})_3$ yet regular in $\text{Nb}(\text{bdt})_3^-$ is probably a consequence of packing forces. The flexibility, afforded by the rotational freedom of the phenyl groups of the tetraphenylarsonium cation, allows effective packing without major deformation of the ligand planes. It is probable then that the structure, observed in the crystal, closely approximates the structure in solution. It is interesting that this bend of the ligand plane from the MS_2 plane has been observed in the trigonal prismatic molybdenum dithiolenes and also in the molybdenum diselenato complex, and now has been observed in $\text{Nb}(\text{bdt})_3^-$, which is isoelectronic with the molybdenum analogue. In contrast, the ligand planes were found to be coplanar with the MS_2 planes in both $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ ¹²⁹ and $\text{V}(\text{S}_2\text{C}_2\text{Ph}_2)_3$.¹³²

A three dimensional representation of the

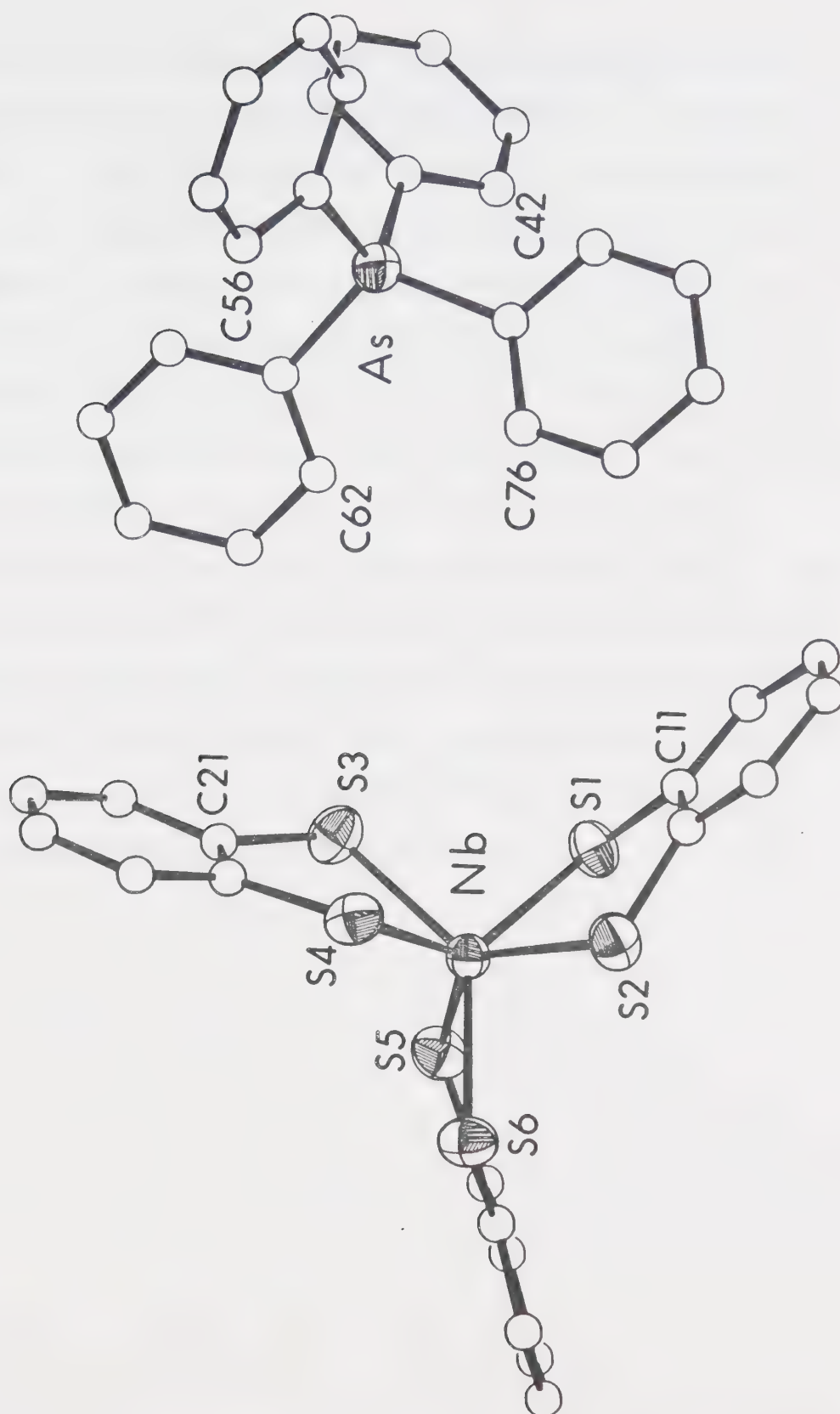


Fig. 16: A PERSPECTIVE VIEW OF $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3]$,
VIEWED DOWN THE CRYSTALLOGRAPHIC b AXIS.

$\text{Nb}(\text{bdt})_3^-$ anion and the tetraphenylarsonium cation, viewed down the crystallographic b axis, is shown in Fig. 16. The geometry of the cation is quite normal with no unusual features. The arsenic atom is surrounded in almost perfect tetrahedral coordination with the C-As-C angles being close to the predicted 109.5° , and all deviations from this value are easily explained by intermolecular interactions. The arsenic-carbon bonds are similar and the mean (1.888 \AA) approximates the value predicted from the sums of the covalent radii^{133,162} (1.94 \AA), assuming an arsenic-carbon single bond involving sp^2 hybridized carbon atoms. These observed bond lengths agree favourably with other determinations^{163,164} where the tetraphenylarsonium cation was involved.

CHAPTER VIII: THE CRYSTAL AND MOLECULAR STRUCTURE
 OF *BIS* (TETRAMETHYLAMMONIUM) *TRIS*
 (BENZENE-1,2-DITHIOLATO) ZIRCONIUM,

$$([(\text{CH}_3)_4\text{N}]_2[\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3]).$$

EXPERIMENTAL

Bright red crystals of $[(\text{CH}_3)_4\text{N}]_2[\text{Zr}(\text{bdt})_3]$, suitable for single crystal X-ray diffraction studies, were kindly supplied by Dr. Takats and Mr. Martin. These crystals were prepared¹⁴³ by the reaction of sodium cyclopentadienide and benzene dithiol and the subsequent reaction with $\text{Zr}[\text{N}(\text{C}_2\text{H}_5)_2]_4$, and crystallization with tetramethylammonium chloride. Preliminary photography showed mmm Laué symmetry indicating an orthorhombic space group. Systematic absences determined by Weissenberg ($0k\ell$, $1k\ell$; CuK_α X-radiation) and Precession photography ($h0\ell$, $h1\ell$, $hk0$, hkl ; MoK_α X-radiation) are $h00$: $h = 2n + 1$, and $0k0$: $k = 2n + 1$ consistent with the space group $\text{P}2_12_12_1$. Precise lattice parameters were obtained at 22° from a least squares analysis performed on the setting angles of 12 high angle reflections, accurately centred on a Picker automatic four circle diffractometer, using CuK_{α_1} X-radiation. The resulting

cell parameters and estimated standard deviations are: $a = 9.931(2) \text{ \AA}$, $b = 14.368(2) \text{ \AA}$, $c = 11.098(2) \text{ \AA}$. The observed density $[1.38(2) \text{ g cm}^{-3}]$, obtained by floatation in a mixture of chloro- and bromo-benzene is consistent with the theoretical value of 1.381 g cm^{-3} , calculated assuming two molecules with formula weight 660.19 a.m.u. occupy the unit cell of volume 1587.9 \AA^3 . Since the space group $P2_12_12$ has four general equivalent positions, the $\text{Zr}(\text{bdt})_3^{2-}$ dianion is therefore restricted to having 2-fold symmetry and must sit on the crystallographic 2-fold axis. The two tetramethylammonium cations can either be related by the two-fold or sit on the two-fold axis.

Intensity data were collected on the Picker automatic diffractometer using CuK_α X-radiation filtered with a 0.0005" thick nickel foil and using a 2° take-off angle. The crystal was mounted in a general orientation but with the a^* axis approximately coincident with the ϕ axis of the diffractometer. A coupled $2\theta/\omega$ scan technique, with a scan speed of 1° min^{-1} , was employed for data collection with all unique reflections with $2\theta \leq 125^\circ$ being collected. The two theta scan range for each reflection was $2^\circ + \Delta 2\theta$ where $\Delta 2\theta$ corresponded to $[2\theta(K_{\alpha_1}) - 2\theta(K_{\alpha_2})]$.

Forty second stationary background counts on each side of the peak were recorded and assuming linearity of background, intensities and standard deviations in the intensities were calculated as shown in Chapter II using a "p factor" of 0.03. A scintillation counter was used in conjunction with a pulse height analyzer, tuned to accept 95% of the CuK_α peak. Three standard reflections were collected automatically every 100 data reflections. In addition several additional reflections were collected manually to assess decomposition. No significant decomposition was observed so no correction was necessary.

Of the 1403 unique reflections collected, 1054 were significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The significant data were then reduced to structure factor amplitudes by correction for Lorentz, polarization and absorption effects. Standard deviations in the structure factors were again calculated as in Chapter II.

The crystal faces were identified and their perpendicular distances to an arbitrarily chosen origin measured as: $(0,1,0)$, 3.268×10^{-3} cm; $(0,\bar{1},0)$, 10.836×10^{-3} cm; $(\bar{1},0,0)$, 20.640×10^{-3} cm; $(0,0,1)$, 3.09×10^{-3} cm; $(1,1,0)$, 0.0 cm; $(1,\bar{1},0)$, 0.0 cm; and $(1,0,\bar{1}2)$, 0.0 cm. The face $(1,0,\bar{1}2)$ is acknow-

ledged as a very unusual choice, but its position is most consistent with the indices chosen, since it is opposite to the $(0,0,1)$ face but inclined to it by about 5° . The absorption coefficient⁸⁶ for CuK_α X-radiation is 66.63 cm^{-1} , leading to a range in transmission factors from 0.756 to 0.423.

In the original data collection several irregularities were observed. These occurred as "pulses" in the counter and their exact cause was unknown, but was probably due to some electronic device connected to the diffractometer power line. The reflections where this was actually observed were rejected. However it was believed (on the basis that several $|F_o|$ values were extremely high) that these pulses had occurred throughout the data collection. For this reason the hkl data were recollected along with the $h\bar{k}l$ data so all three data sets could be compared and faulty reflections could be excluded. The second hkl data set was merged with the $h\bar{k}l$ data to obtain improved standard deviations. In this merged data set the number of statistically reliable reflections increased to 1126. The same data collection techniques were used for the second hkl data and the $h\bar{k}l$ data as was used for the original hkl data. Terms used in the Zachariasen extinction correction were calculated at this stage.

STRUCTURE SOLUTION AND REFINEMENT

A sharpened Patterson map¹⁴⁶ was computed between the limits $0 \leq u \leq 0.5$, $0 \leq v \leq 0.5$, $0 \leq w \leq 0.5$. Since the zirconium atom is restricted to lie on the two-fold axis, the Harker vectors are located at $1/2, 1/2, 2z$; and $1/2, 1/2, -2z$, so the solution is trivial yielding the coordinates for the zirconium as $(0.0, 0.0, 0.189)$ from the largest vector at $(0.5, 0.5, 0.378)$. The next six most intense vectors could be interpreted as Zr-S vectors about either the origin or the Zr-Zr Harker vector. From initial inspection of the placement of these vectors, it was evident that the zirconium coordination was close to octahedral and was definitely not trigonal prismatic. Due to the extra symmetry of the Patterson, care had to be taken in choosing the vectors to represent the three independent sulfur atoms, in order for the model to phase correctly. Several arbitrary choices can be made initially. The S1 position was calculated from the vector at $(0.05, 0.168, 0.0)$ yielding the coordinates $(0.05, 0.168, 0.189)$. From the vector at $(0.16, 0.0, 0.18)$ the S2 position was calculated as $(0.16, 0.0, 0.009)$. The position of S3, however, must be chosen in such a way to be consistent with the choice of S1 and S2. There are two

possible choices for the S3 position yielding the positions (0.185, -0.048, 0.315) or (0.185, 0.048, 0.315). A choice between the two was made on the basis of sulfur-sulfur vectors which showed the first position was correct.

In the first refinements, involving only the zirconium and sulfur positions, the y coordinate of S2 was not refined, since it was possible that it could refine in the wrong direction and hamper the phasing. A brief resumé of the refinement is shown in Table 39.

TABLE 39: REFINEMENT OUTLINE

MODEL	R_1	R_2
(1) Zr and S atoms	0.297	0.384
(2) Complete anion (isotropic B's)	0.152	0.243
(3) Anion and Cation (isotropic B's)	0.088	0.106
(4) Anisotropic Zr and S	0.074	0.097
(5) Anisotropic Zr, S, N and C atoms of tetramethyl ammonium	0.069	0.088
(6) Absorption Correction	0.050	0.063
(7) Change of Hand	0.057	0.073
(8) Carbon atoms of dithiolene ligands anisotropic	0.042	0.061
(9) Hydrogen atoms of dithiolene ligands	0.039	0.059
(10) Extinction correction ¹⁴⁷	0.039	0.059
(11) Merged Data	0.034	0.053
(12) Methyl Hydrogens included as rotors	0.029	0.035

Structure factors were calculated using the atomic scattering factors for the neutral atoms for zirconium, sulfur, carbon and nitrogen by Cromer and Mann.⁷⁵ The scattering factors for hydrogen were those of Stewart, Davidson and Simpson.¹⁴⁹ Anomalous dispersion corrections by Cromer⁷⁶ were applied to the zirconium and sulfur scattering factors ($\Delta f'_{\text{Zr}} = -0.62$, $\Delta f''_{\text{Zr}} = 2.42$, $\Delta f'_{\text{S}} = 0.31$, $\Delta f''_{\text{S}} = 0.58$).

A refinement was performed with a change of hand for model (6) and the original model was judged significantly better on the basis of a Hamilton's R test⁷⁹ (at the 0.005 significance level). Hydrogen positions on the dithiolene ligands were calculated from the known geometry and orientation of the benzene rings, using a C-H distance of 1.0 Å. The hydrogen parameters were not refined. The hydrogen atoms were given thermal parameters approximately 10 - 15% greater than their attached carbon atom. An electron density difference map, phased on model (11), failed to locate any of the methyl hydrogen atoms, instead only smears of electron density were observed in the predicted regions. In addition the tetramethylammonium carbon atoms had anomalous thermal parameters, so the difference map was inspected for obvious signs of

disorder involving these carbon atoms. No signs of disorder, however, were obvious. Although the methyl hydrogens were not located, they were added to the structure factor calculations in the form of free rotating rigid bodies.¹⁶⁵ The ideal tetrahedral coordination of the carbon atoms was assumed and the centres of gravity and angles defining the orientation of the "hydrogen triangles" were calculated using the assumed geometry, and the direction cosines of the nitrogen-carbon bonds.

Model (11), which is the refinement of the merged data, contains all the corrections performed on the previous models.

RESULTS

Observed and calculated structure factor amplitudes, $|F_o|$ and $|F_c|$, are shown in Table 40. The final fractional coordinates and isotropic temperature factors of all atoms are shown in Table 41. Standard deviations were obtained from the inverse matrix of the final least squares analysis. Table 42 shows the anisotropic thermal parameters (U_{ij} 's)⁸⁰ of all anisotropic atoms. Relevant bond lengths and angles are shown in Tables 43 and 44, and were obtained with

their standard deviations from ORFFE. Several inter-ionic contacts which are comparable to the predicted van der Waals contacts¹⁵¹ are shown in Table 45. Selected least squares planes are shown in Table 46. In addition Table 47 lists the dihedral angles between selected planes.

The numbering scheme for all non-hydrogen atoms is shown in Figures 17 and 18. The hydrogen atoms H1 through H6 are attached sequentially to the carbon atoms (C2 through C9) which are not bonded to sulfur atoms. The hydrogen atoms H7 through H18 are bonded sequentially in groups of three to carbon atoms C10 through C13. Since the hydrogen atoms of the methyl groups were included as hindered rotors, no individual temperature factors are given, rather the temperature factors for the groups are shown in Table 41.

TABLE 40: OBSERVED AND CALCULATED STRUCTURE
FACTOR AMPLITUDES (ELECTRONS X 10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 0**				7	1	148	148	1	1	538	514	7	6	262	256	1	6	414	421
C	1	507	553	7	2	495	493	1	2	962	955	7	7	151	150	1	7	150	145
C	2	797	721	7	3	312	307	1	3	533	537	7	8	159	140	1	9	399	393
0	3	114	111	7	4	427	429	1	5	635	628	7	10	183	195	1	10	259	255
0	4	217	214	7	5	177	167	1	6	566	562	7	11	158	165	1	11	186	175
0	5	784	806	7	6	569	570	1	7	343	338	8	1	167	164	1	12	113	110
0	6	967	1008	7	7	216	216	1	8	264	254	8	2	306	309	2	0	93	31
0	7	402	407	7	8	135	144	1	9	205	204	8	3	152	157	2	1	236	228
0	8	106	167	7	9	137	148	1	10	265	262	8	4	378	381	2	2	260	256
0	9	554	545	7	10	167	185	1	11	164	168	8	5	151	148	2	3	1075	1047
0	10	190	189	7	11	214	230	2	1	314	265	8	6	141	146	2	4	393	390
0	11	117	106	8	0	388	381	2	2	939	936	8	7	261	261	2	5	374	384
1	1	1146	1184	8	1	632	642	2	3	399	400	8	8	193	209	2	7	138	147
1	2	345	319	8	3	206	204	2	4	581	595	8	9	206	214	2	8	290	278
1	3	400	402	8	4	197	198	2	5	246	259	8	10	163	166	2	9	271	272
1	4	216	225	8	5	419	417	2	6	265	261	9	0	343	344	2	10	165	172
1	5	167	167	8	6	147	132	2	7	408	417	9	1	207	214	2	11	273	250
1	6	718	727	8	7	191	179	2	8	222	228	9	3	107	114	3	0	146	152
1	7	712	709	8	10	202	202	2	9	192	197	9	5	143	153	3	1	258	263
1	9	201	214	9	1	106	107	2	10	213	203	9	6	248	245	3	2	158	163
1	11	178	184	9	2	285	291	2	11	106	98	9	8	141	154	3	4	601	604
1	12	240	239	9	4	258	256	2	12	234	224	9	10	114	124	3	5	151	150
2	0	420	427	9	7	317	304	3	0	1585	1617	10	1	137	135	3	6	205	190
2	1	726	686	9	8	231	242	3	1	542	532	10	2	224	223	3	7	192	178
2	2	296	311	9	9	144	138	3	2	240	242	10	3	167	160	3	8	94	88
2	3	658	671	9	10	144	155	3	4	278	261	10	4	233	222	3	9	306	307
2	4	266	279	10	0	414	397	3	5	330	325	10	6	243	227	3	10	391	389
2	5	680	657	10	1	337	331	3	6	523	526	10	7	218	215	3	12	165	177
2	6	589	582	10	3	347	345	3	7	145	143	10	8	108	112	4	0	118	60
2	8	217	211	10	4	151	128	3	8	173	150	10	9	149	155	4	1	477	479
2	9	188	181	10	5	305	300	3	10	83	99	11	0	441	444	4	2	515	520
2	10	223	209	10	6	214	213	3	11	248	249	11	1	265	262	4	3	595	614
2	11	223	222	11	1	156	143	3	12	98	88	11	2	205	202	4	4	471	465
2	12	158	143	11	2	397	405	4	0	335	319	11	3	335	335	4	5	168	164
3	1	376	377	11	3	166	156	4	1	271	280	11	4	177	173	4	6	209	212
3	2	154	111	11	4	478	469	4	2	307	292	11	5	409	396	4	7	141	150
3	3	221	233	11	5	144	141	4	3	387	403	11	7	111	100	4	8	379	381
3	5	235	253	11	6	281	288	4	4	210	198	11	8	119	122	4	9	174	162
3	6	214	218	11	7	94	112	4	5	151	149	12	0	143	160	4	10	183	177
3	7	662	675	11	8	96	98	4	6	445	440	12	1	282	279	4	11	177	181
3	8	214	210	11	9	147	167	4	7	521	517	12	2	258	266	5	0	125	130
3	9	221	213	12	0	395	390	4	8	154	141	12	3	189	202	5	1	554	564
3	10	174	169	12	1	279	295	4	9	279	279	12	4	355	353	5	2	635	630
3	12	300	309	12	2	163	164	4	10	151	156	12	6	278	275	5	3	491	487
4	0	1678	1630	12	3	287	281	4	11	130	150	12	7	132	139	5	4	645	642
4	1	754	734	12	4	159	160	4	12	209	218	13	0	328	332	5	5	217	210
4	2	213	208	12	5	397	393	5	0	1388	1371	13	1	169	167	5	6	295	303
4	3	178	188	12	7	85	95	5	1	613	615	13	2	152	149	5	7	323	312
4	4	131	126	13	1	106	107	5	2	580	561	13	3	176	169	5	8	168	172
4	5	253	262	13	2	128	124	5	3	379	370	13	5	171	171	5	9	391	387
4	6	734	736	13	3	97	107	5	4	383	378	13	6	111	128	5	10	136	137
4	8	160	157	13	4	183	173	5	5	692	692	14	0	121	119	5	11	125	138
4	9	142	147	13	6	192	206	5	6	299	310	14	4	97	111	6	0	764	785
4	10	186	199	13	7	121	121	5	7	283	285	15	1	90	73	6	1	266	269
4	11	159	170	14	0	180	184	5	8	320	333	16	0	73	77	6	2	799	806
4	12	79	83	14	1	128	122	5	9	135	150	16	1	84	82	6	3	551	541
5	1	566	590	14	3	112	101	5	10	311	303	**H = 2****				6	4	175	174
5	2	426	432	14	5	90	113	5	11	162	160	0	0	1160	1162	6	5	382	378
5	3	177	185	14	6	84	103	6	0	293	287	0	1	919	978	6	6	179	179
5	4	587	576	15	2	132	118	6	1	743	725	0	2	1375	1394	6	7	333	332
5	6	381	386	15	4	96	91	6	2	478	487	0	3	783	793	6	8	307	311
5	7	487	485	16	0	181	179	6	3	351	335	0	4	139	147	6	10	162	157
5	8	88	67	16	1	93	108	6	4	738	740	0	5	620	631	6	11	129	134
5	9	263	255	**H = 1****				6	5	163	160	0	6	101	63	7	1	528	520
5	11	216	218	0	1	682	709	6	6	567	581	0	7	287	288	7	2	180	177
6	0	1670	1703	0	2	659	672	6	7	322	339	0	8	349	336	7	3	372	370
6	1	373	380	0	3	514	534	6	8	192	198	0	10	239	230	7	4	581	572
6	2	343	351	0	4	623	610	6	9	282	288	0	11	105	90	7	5	220	214
6	3	266	270	0	5	115	94	6	10	154	149	0	12	124	127	7	6	352	344
6	4	430	430	0	6	808	794	6	11	182	196	1	0	385	369	7	7	238	235
6	5	865	846	0	7	643	625	7	0	671	677	1	1	676	675	7	9	264	261
6	6	298	305	0	8	282	281	7	1	443	435	1	2	972	967	7	10	180	173
6	7	244	241	0	9	397	404	7	2	432	441	1	3	767	765	8	0	345	340
6	9	202	192	0	11	192	190	7	3	503	503	1	4	1042	1060	8	1	107	110
6	10	269	266	0	12	206	208	7	4	171	173	1	5	269	267	8	2	229	226
6	11	166	171	1	0	1585	1547	7	5	500	490								

Table 40 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 2**				1	9	289	282	8	8	131	115	2	6	288	284	9	9	99	127
8	3	261	258	1	10	202	202	8	9	217	215	2	7	203	199	10	0	303	315
8	4	163	173	1	11	171	168	8	10	131	146	2	8	444	442	10	1	180	199
8	5	199	191	2	0	535	533	9	0	223	228	2	9	186	190	10	2	174	180
8	6	225	211	2	1	124	114	9	1	182	177	2	10	162	157	10	3	382	382
8	7	127	138	2	2	594	592	9	2	377	380	2	11	125	129	10	4	139	134
8	8	252	259	2	3	355	326	9	3	92	77	3	0	410	400	10	5	127	130
8	9	112	92	2	4	889	887	9	4	352	349	3	1	372	368	10	6	183	182
8	10	84	90	2	5	247	234	9	6	213	212	3	2	267	263	10	7	103	98
9	1	316	307	2	6	164	155	9	7	187	191	3	3	446	434	10	8	189	190
9	3	92	98	2	7	137	151	9	8	242	238	3	4	358	362	11	0	181	177
9	4	110	121	2	9	367	363	9	9	100	82	3	5	276	282	11	1	217	215
9	5	299	297	2	10	344	339	10	0	153	148	3	6	342	343	11	2	205	204
9	6	133	131	2	11	88	96	10	1	369	371	3	7	189	191	11	3	135	140
9	7	259	254	3	1	131	138	10	2	170	158	3	8	136	123	11	4	226	226
9	8	91	109	3	2	548	565	10	3	153	154	3	9	280	280	11	5	131	140
9	9	186	187	3	3	718	711	10	4	179	182	3	10	211	199	11	6	155	142
9	10	117	127	3	4	540	526	10	5	136	160	3	11	90	87	11	7	109	112
10	0	386	381	3	5	240	240	10	6	213	188	4	0	130	119	12	2	214	216
10	1	155	147	3	7	171	169	10	7	214	211	4	1	306	297	12	3	183	178
10	2	375	370	3	8	244	242	10	8	148	160	4	2	460	473	12	5	172	162
10	3	220	223	3	9	365	359	10	9	192	192	4	3	550	554	12	7	109	108
10	4	293	292	3	10	88	92	11	0	296	288	4	4	376	386	13	1	162	170
10	5	122	112	3	11	189	188	11	1	128	120	4	5	297	289	13	2	151	154
10	6	233	236	4	0	115	126	11	2	357	354	4	6	286	291	13	3	157	159
10	7	140	129	4	1	587	600	11	3	255	265	4	7	256	251	13	4	161	163
10	8	242	235	4	2	403	402	11	5	117	119	4	8	382	383	14	0	105	116
11	1	363	356	4	3	300	299	11	6	158	166	4	9	150	158	14	2	105	122
11	2	215	208	4	4	641	636	11	7	219	205	4	10	119	123	14	3	163	155
11	3	213	223	4	5	294	287	11	8	231	235	4	11	193	191	14	4	117	101
11	4	306	309	4	6	257	256	12	0	87	89	5	0	69	52	15	0	93	99
11	5	106	93	4	7	142	144	12	1	367	364	5	1	616	610	15	1	127	130
11	6	182	180	4	9	321	317	12	2	175	175	5	2	449	443	**H = 5****			
11	7	186	187	4	10	236	236	12	3	175	170	5	3	323	344	0	1	672	675
11	8	131	133	5	0	117	113	12	4	215	212	5	4	549	549	0	2	101	98
12	0	335	338	5	1	210	206	12	5	132	130	5	5	305	300	0	4	107	96
12	2	293	294	5	2	673	668	12	6	132	135	5	6	204	196	0	5	273	288
12	3	237	235	5	3	746	743	12	7	143	155	5	7	223	229	0	6	294	284
12	5	160	151	5	4	164	164	13	0	217	215	5	9	233	246	0	7	475	459
12	6	157	139	5	5	211	217	13	2	228	228	5	10	142	151	0	8	118	114
12	7	180	189	5	6	134	136	13	3	184	186	6	0	404	400	0	9	173	168
13	0	206	217	5	7	332	350	13	4	123	120	6	1	285	288	0	11	82	88
13	1	223	221	5	8	439	450	13	6	132	129	6	2	457	465	1	0	652	664
13	2	93	82	5	9	133	120	14	1	119	120	6	3	546	536	1	1	330	331
13	3	126	134	5	10	159	157	14	4	93	113	6	4	123	127	1	2	331	323
13	4	152	154	5	11	108	105	14	5	94	105	6	5	224	230	1	3	184	189
13	5	126	98	6	0	99	99	15	2	84	94	6	6	167	185	1	4	228	240
13	6	148	140	6	1	461	461	15	3	89	93	6	7	217	207	1	5	396	382
13	7	144	148	6	2	261	267	**H = 4****				6	8	342	338	1	6	509	514
14	0	133	133	6	3	513	518	0	0	435	439	6	9	95	100	1	7	196	203
14	2	89	114	6	4	521	522	0	2	532	524	6	10	112	119	1	8	330	341
14	3	90	92	6	5	143	143	0	3	735	734	7	0	414	420	1	10	157	159
14	4	98	77	6	6	334	326	0	4	124	117	7	1	370	380	1	11	149	153
15	1	85	88	6	7	233	223	0	5	209	196	7	2	391	398	2	0	366	368
15	2	85	80	6	8	247	247	0	6	268	249	7	3	210	213	2	1	720	721
15	3	94	92	6	9	367	371	0	7	271	270	7	4	320	317	2	2	393	390
15	4	82	92	6	10	117	117	0	8	417	422	7	6	272	258	2	3	179	172
H = 3**				6	11	73	36	0	9	147	134	7	7	284	285	2	4	160	140
0	1	329	334	7	0	282	286	0	10	178	159	7	8	97	121	2	5	285	265
0	2	893	894	7	1	279	281	0	11	95	93	7	9	235	255	2	6	293	281
0	3	705	725	7	2	516	526	1	0	199	203	7	10	85	91	2	7	507	498
0	4	890	902	7	3	611	607	1	1	710	717	8	1	293	293	2	9	140	157
0	6	332	314	7	4	346	341	1	2	490	486	8	2	347	343	2	11	81	65
0	8	150	141	7	5	88	131	1	3	335	312	8	3	262	251	3	0	883	890
0	9	519	522	7	6	166	165	1	4	630	622	8	5	259	254	3	1	335	336
0	10	248	244	7	7	241	234	1	5	233	230	8	6	144	149	3	2	416	418
0	11	136	132	7	8	375	380	1	6	219	216	8	7	192	197	3	3	201	204
1	0	459	470	7	9	103	87	1	7	341	334	8	8	280	288	3	4	121	128
1	1	317	317	7	10	88	89	1	9	320	318	8	9	118	138	3	5	336	329
1	2	632	631	8	0	352	347	1	10	109	112	9	1	360	364	3	6	420	415
1	3	1339	1356	8	1	427	429	2	0	67	90	9	2	180	178	3	7	147	155
1	4	341	349	8	2	245	251	2	1	495	489	9	3	142	130	3	8	268	272
1	5	403	389	8	3	109	101	2	2	564	581	9	4	304	301	3	10	134	133
1	6	199	197	8	4	270	256	2	3	537	526	9	5	178	170	4	0	223	221
1	7	224	221	8	5	319	315	2	4	266	275	9	6	151	159	4	1	620	627
1	8	495	501	8	7	190	206	2	5	301	295	9	7	136	148				

Table 40 (continued)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL
H = 5**				C	3	141	133	9	4	280	279	7	4	149	155	10	0	221	215
4	2	347	339	0	5	481	490	9	6	149	154	7	5	275	281	10	2	176	186
4	3	178	172	0	6	480	468	9	7	127	126	7	6	231	228	10	3	126	123
4	4	295	301	0	8	119	113	10	0	149	154	7	8	141	134	11	1	174	171
4	5	261	247	0	10	128	133	10	1	328	331	8	1	320	317	**H = 9****			
4	6	263	263	1	1	601	605	10	3	235	218	8	2	164	175	C	2	151	145
4	7	333	327	1	2	174	175	10	4	155	148	8	3	124	122	0	4	245	238
4	8	114	112	1	3	192	179	10	5	282	284	8	4	249	241	1	0	86	79
4	9	134	143	1	4	156	149	10	6	102	84	8	5	98	103	1	2	221	217
4	10	110	102	1	5	333	329	11	2	178	168	8	6	121	127	1	3	351	347
5	0	252	263	1	6	335	341	11	4	145	158	8	7	157	168	2	1	314	331
5	1	244	255	1	7	370	367	11	5	81	44	9	0	281	285	2	2	242	250
5	2	155	165	2	0	808	823	12	0	164	151	9	1	118	135	2	3	153	145
5	3	149	153	2	1	197	197	12	1	132	136	9	2	169	177	2	4	308	301
5	4	254	238	2	2	160	174	12	4	80	93	9	3	149	157	2	5	111	112
5	5	464	462	2	3	111	125	13	0	120	118	9	4	175	172	2	6	90	110
5	6	228	235	2	4	339	343	13	1	101	94	9	5	269	273	3	0	252	251
5	7	134	130	2	5	461	460	13	2	160	163	9	6	113	105	3	1	123	112
5	8	250	250	2	6	465	469	**H = 7****				10	1	191	191	3	2	378	371
5	10	166	171	2	7	147	160	0	2	119	127	10	2	175	170	3	3	397	398
6	0	86	107	2	8	229	223	0	4	274	274	10	3	98	95	3	5	191	185
6	1	297	300	2	9	124	128	0	6	181	173	10	4	105	120	3	7	204	191
6	2	229	228	2	10	168	167	0	7	146	148	11	0	228	224	4	0	100	87
6	3	102	102	3	1	477	494	0	8	88	92	12	0	120	117	4	1	198	203
6	4	292	299	3	2	181	182	0	9	129	136	12	1	120	137	4	2	147	142
6	6	251	257	3	3	192	193	1	0	255	260	**H = 8****				4	3	189	190
6	7	290	283	3	4	219	218	1	1	202	209	0	1	140	127	4	4	291	278
6	9	150	143	3	6	275	275	1	2	158	134	0	3	522	531	4	6	138	149
6	10	86	94	3	7	388	384	1	3	213	208	0	5	139	149	5	1	106	89
7	0	348	354	3	8	95	98	1	4	262	268	0	7	85	91	5	2	222	219
7	1	319	337	3	9	162	157	1	5	446	448	0	8	104	120	5	3	219	206
7	2	107	115	3	10	71	64	1	6	214	213	1	2	327	320	5	4	124	117
7	3	390	384	4	0	486	496	1	9	86	79	1	3	134	138	5	5	106	85
7	5	338	342	4	1	462	473	2	1	473	471	1	4	375	362	6	0	102	104
7	6	254	254	4	2	176	166	2	2	391	385	2	2	332	334	6	2	127	120
7	8	201	211	4	3	161	150	2	3	214	202	2	3	323	328	6	3	93	91
7	9	96	115	4	4	193	200	2	4	360	364	2	4	131	135	6	4	102	117
8	0	209	214	4	5	473	483	2	5	174	164	2	5	333	327	6	5	153	134
8	1	278	281	4	6	335	338	2	6	230	206	2	7	160	170	7	0	84	85
8	2	470	465	4	7	106	93	2	7	193	197	2	8	187	184	7	2	212	201
8	4	304	291	4	8	212	221	2	9	121	120	3	1	278	275	7	3	184	186
8	6	140	150	4	10	184	187	3	0	574	582	3	2	267	267	7	4	93	92
8	7	208	202	5	0	326	320	3	1	337	337	3	3	236	246	8	0	92	89
8	8	85	82	5	1	364	366	3	2	278	278	3	4	424	425	8	1	261	262
8	9	115	126	5	2	375	384	3	3	310	319	3	6	204	201	8	2	91	80
9	0	137	143	5	4	182	185	3	4	258	249	3	8	84	85	8	3	116	106
9	1	185	184	5	5	183	188	3	5	471	470	4	0	220	218	8	4	196	201
9	2	130	124	5	6	229	214	3	6	163	152	4	1	130	106	9	0	195	191
9	3	277	271	5	7	224	226	3	7	96	107	4	2	242	245	9	2	230	228
9	4	195	186	5	8	124	128	3	8	154	174	4	3	419	416	**H = 10****			
9	5	309	310	5	9	116	134	3	9	89	79	4	5	220	230	0	2	161	157
9	8	130	130	6	0	436	436	4	0	282	294	4	7	132	125	0	3	131	149
10	0	230	237	6	1	258	256	4	1	271	263	4	8	145	140	0	4	150	124
10	1	115	108	6	4	220	216	4	2	339	336	5	1	165	160	1	1	191	192
10	2	243	242	6	5	394	394	4	3	168	169	5	2	159	168	1	5	97	111
10	4	284	279	6	6	271	268	4	4	286	278	5	4	253	240	2	0	262	262
10	5	187	175	6	7	103	95	4	6	247	253	5	5	164	155	2	2	274	276
10	6	181	177	6	8	107	112	4	7	218	203	5	7	101	110	2	3	170	157
10	7	103	119	7	1	233	222	4	9	179	184	6	2	120	120	2	5	120	116
11	0	119	108	7	2	206	217	5	0	239	239	6	3	129	133	3	1	309	313
11	1	241	242	7	3	223	223	5	1	255	253	6	5	99	85	3	2	94	107
11	3	220	220	7	4	205	196	5	3	121	108	6	6	98	124	3	3	163	161
11	4	121	105	7	5	185	173	5	4	159	160	7	1	192	206	3	4	190	201
11	5	261	254	7	6	217	211	5	5	326	340	7	3	125	118	4	0	182	173
12	1	150	168	7	7	218	219	5	6	186	183	7	4	145	147	4	2	226	224
12	2	219	229	7	9	107	112	5	8	185	173	7	5	161	167	4	3	211	211
12	4	190	195	8	0	333	325	6	1	215	222	7	6	85	84	5	0	97	95
13	0	126	131	8	1	249	251	6	2	181	166	8	0	310	307	5	1	116	122
13	1	136	127	8	2	123	118	6	3	145	135	8	2	273	262	5	2	140	138
13	3	193	193	8	3	212	222	6	4	153	162	8	3	137	141	6	1	87	65
13	4	121	111	8	4	319	320	6	5	176	189	8	5	174	178	6	2	104	101
14	1	102	93	8	5	391	386	6	6	104	111	8	6	98	105	7	1	111	122
14	2	128	137	8	6	150	153	6	7	199	208	9	1	314	313	**H = 11****			
H = 6**				8	8	130	131	7	0	310	320	9	2	105	100	C	1	117	118
0	0	765	769	9	1	228	224	7	1	173	169	9	3	136	129	1	0	233	236
C	1	381	389	9	2	371	373	7	2	232	238	9	4	196	196	2	1	264	278
0	2	103	100	9	3	106	99	7	3	183	155								

TABLE 41: ATOM COORDINATES AND ISOTROPIC
TEMPERATURE FACTORS

Atom	x	y	z	B
Zr	0.0	0.0	-0.18983(6)	3.01*
S1	-0.1645(2)	-0.0080(2)	-0.0132(1)	4.56*
S2	0.0535(2)	0.1716(1)	-0.2142(2)	4.15*
S3	-0.1851(2)	0.0474(1)	-0.3350(1)	4.33*
C1	-0.0697(7)	-0.0046(7)	0.1207(5)	4.55*
C2	-0.1364(10)	-0.0100(8)	0.2326(6)	7.08*
C3	-0.0686(11)	-0.0036(10)	0.3391(5)	8.76*
C4	-0.0580(7)	0.2186(4)	-0.3220(5)	3.71*
C5	-0.0480(8)	0.3120(5)	-0.3527(6)	5.13*
C6	-0.1351(10)	0.3523(6)	-0.4355(7)	6.07*
C7	-0.2330(10)	0.2999(8)	-0.4869(8)	6.57*
C8	-0.2475(8)	0.2068(6)	-0.4570(6)	5.08*
C9	-0.1597(7)	0.1658(5)	-0.3737(5)	3.93*
N	-0.4980(8)	-0.2008(3)	-0.1384(5)	4.45*
C10	-0.3933(9)	-0.2662(8)	-0.1198(14)	10.92*
C11	-0.5023(15)	-0.1388(7)	-0.0264(8)	10.01*
C12	-0.4761(11)	-0.1372(7)	-0.2393(8)	9.07*
C13	-0.6332(9)	-0.2452(6)	-0.1408(10)	7.08*
<u>RIGID BODIES</u>				
H1	-0.2398	-0.0170	0.2308	7.90
H2	-0.1198	-0.0085	0.4177	9.60

Table 41 (continued)

Atom	x	y	z	B
D	4.610 ^a			
E	1.571			
F	1.571			
H3	0.0269	0.3512	-0.3143	6.20
H4	-0.1241	0.4203	-0.4566	7.00
H5	-0.2981	0.3283	-0.5469	7.90
H6	-0.3209	0.1671	-0.4949	6.30
D	3.391			
E	2.447			
F	3.747			

HINDERED ROTORS

H7	-0.3503	-0.2810	-0.1985	11.00
H8	-0.3250	-0.2381	-0.0636	
H9	-0.4316	-0.3238	-0.0827	
BARRIER	0.02 ^b			
RADIUS	0.946			
D	0.721			
E	1.373			
F	0.0			
H10	-0.5980	-0.1260	-0.0060	11.00
H11	-0.4537	-0.0797	-0.0446	
H12	-0.4571	-0.1722	0.0416	
BARRIER	0.02			

Table 41 (continued)

ATOM	x	y	z	B
RADIUS	0.946			
D	0.625			
E	3.106			
F	0.0			
H13	-0.3775	-0.1230	-0.2447	9.5
H14	-0.5275	-0.0785	-0.2238	
H15	-0.5078	-0.1674	-0.3144	
BARRIER	0.02			
RADIUS	0.946			
D	0.676			
E	6.091			
F	0.0			
H16	-0.6652	-0.2550	-0.0568	8.0
H17	-0.6972	-0.2034	-0.1853	
H18	-0.6265	-0.3065	-0.1838	
BARRIER	0.02			
RADIUS	0.946			
D	0.444			
E	4.689			
F	0.0			

*Equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 42.

^aD, E, and F are as described for Table 32.

^bBARRIER (Bd) is the relative barrier to rotation of the hindered rotor group. $Bd = V_0/2kT$, where V_0 = potential barrier to rotation (kcal mol^{-1}).

TABLE 42: ANISOTROPIC THERMAL PARAMETERS (\AA^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0369(4)	0.0467(4)	0.0309(3)	0.0033(5)	0.0	0.0
Si	0.0519(10)	0.0724(12)	0.0491(8)	-0.0014(13)	0.0142(8)	-0.0058(13)
S2	0.0503(10)	0.0535(9)	0.0536(10)	-0.0022(8)	-0.0099(8)	0.0043(8)
S3	0.0479(10)	0.0663(10)	0.0502(10)	0.0035(9)	-0.0149(9)	-0.0029(8)
Cl	0.093(5)	0.042(3)	0.038(3)	-0.021(6)	0.013(3)	-0.003(5)
C2	0.134(8)	0.080(6)	0.055(4)	-0.051(6)	0.042(5)	-0.029(5)
C3	0.200(12)	0.096(5)	0.036(3)	-0.065(11)	0.021(4)	-0.015(7)
C4	0.049(4)	0.055(4)	0.038(3)	0.009(3)	0.004(3)	0.005(3)
C5	0.074(6)	0.061(4)	0.060(4)	0.011(4)	0.012(4)	0.009(4)
C6	0.080(6)	0.080(6)	0.071(5)	0.033(5)	0.011(5)	0.024(5)
C7	0.081(7)	0.116(7)	0.052(5)	0.044(6)	-0.004(5)	0.026(6)
C8	0.058(5)	0.088(6)	0.047(4)	0.022(4)	-0.012(4)	0.014(5)
C9	0.049(4)	0.070(4)	0.030(3)	0.018(4)	0.005(3)	0.002(3)
N	0.042(3)	0.054(3)	0.073(3)	-0.005(4)	-0.000(5)	0.017(3)

Table 42 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C10	0.048(6)	0.110(8)	0.257(16)	0.028(5)	0.031(8)	0.081(10)
C11	0.153(10)	0.113(7)	0.114(7)	-0.049(9)	-0.003(11)	-0.018(6)
C12	0.083(8)	0.137(8)	0.124(7)	-0.012(6)	0.006(6)	0.075(7)
C13	0.063(6)	0.095(7)	0.111(8)	-0.018(5)	-0.009(6)	0.032(6)

TABLE 43: INTRA-IONIC CONTACTS ($\overset{\circ}{\text{\AA}}$)

ATOMS	DISTANCE ($\overset{\circ}{\text{\AA}}$)	ATOMS	DISTANCE ($\overset{\circ}{\text{\AA}}$)
Zr-S1	2.555(2)	Zr-S2	2.537(2)
Zr-S3	2.538(2)	S2-S3	3.255(2)
S1-S1'	3.275(3)	S1-S2'	3.424(3)
S2-S3'	3.662(2)	S1-S3	3.665(2)
S1-C1	1.759(6)	S2-C4	1.764(6)
S3-C9	1.772(7)	C1-C1'	1.391(14)
C1-C2	1.410(8)	C2-C3	1.364(11)
C3-C3'	1.366(22)	C4-C5	1.388(9)
C5-C6	1.389(10)	C6-C7	1.355(13)
C7-C8	1.386(11)	C8-C9	1.400(9)
C9-C4	1.388(9)	N-C10	1.416(10)
N-C11	1.530(10)	N-C12	1.462(9)
N-C13	1.487(10)		

TABLE 44: INTRA-IONIC ANGLES (DEGREES)

ATOMS	ANGLE	ATOMS	ANGLE
S1-Zr-S1'	79.74 (8)	S2-Zr-S3	79.80 (6)
S1-Zr-S3	92.06 (6)	S1-Zr-S2'	84.51 (7)
S3-Zr-S2'	92.40 (6)	S3-Zr-S3'	101.19 (8)
S1-Zr-S2	105.03 (7)	S2-Zr-S2'	167.76 (8)
S1-Zr-S3'	159.80 (7)	Zr-S1-C1	107.7 (2)
Zr-S2-C4	108.2 (2)	Zr-S3-C9	108.0 (2)
S1-C1-C1'	122.4 (2)	S2-C4-C9	121.9 (5)
S3-C9-C4	121.8 (5)	C1'-C1-C2	118.2 (5)
C1-C2-C3	121.8 (9)	C2-C3-C3'	119.9 (6)
C9-C4-C5	118.6 (6)	C4-C5-C6	121.4 (7)
C5-C6-C7	119.6 (8)	C6-C7-C8	120.7 (8)
C7-C8-C9	119.9 (8)	C8-C9-C4	119.8 (6)
C10-N-C11	106.8 (10)	C10-N-C12	114.7 (8)
C10-N-C13	112.4 (6)	C11-N-C12	105.1 (6)
C11-N-C13	103.8 (8)	C12-N-C13	112.9 (7)
S2'-S1-S3	62.10 (5)	S2'-S3-S1	55.71 (5)
S1'-S2-S3'	62.19 (5)		

TABLE 45: INTER-IONIC CONTACTS (\AA)

ATOM 1	ATOM 2	SYMMETRY OPERATION ON ATOM 2	DISTANCE (\AA)
S2	H5	$1/2+x, 1/2-y, \bar{z}-1$	3.031
S2	C10	\bar{x}, \bar{y}, z	3.786(9)
S3	H2	$x, y, z-1$	2.930
S3	C12	$\bar{x}-1, \bar{y}, z-1$	3.756(11)
C1	C10	$1/2-x-1, 1/2+y, \bar{z}$	3.446(15)
C1	C13	$1/2+x, 1/2-y-1, \bar{z}$	3.657(13)
C1	C10	$1/2+x, 1/2-y-1, \bar{z}$	3.730(15)
C2	C13	$1/2+x, 1/2-y-1, \bar{z}$	3.662(14)
C2	C10	$1/2-x-1, 1/2+y, \bar{z}$	3.733(17)
C3	C6	$1/2-x-1, 1/2+y-1, \bar{z}$	3.754(12)
C4	H5	$1/2+x, 1/2-y, \bar{z}-1$	3.036
C4	C13	$\bar{x}-1, \bar{y}, z$	3.687(12)
C5	H6	$1/2+x, 1/2-y, \bar{z}-1$	2.832
C5	C8	$1/2+x, 1/2-y, \bar{z}-1$	3.666(10)
C8	C13	$\bar{x}-1, \bar{y}, z$	3.745(13)
C8	C12	$\bar{x}-1, \bar{y}, z$	3.792(13)
C9	C13	$\bar{x}-1, \bar{y}, z$	3.494(12)

TABLE 46: LEAST SQUARES PLANE CALCULATIONS

(A) ATOMS FORMING PLANE: Zr, S1, S3

$$\text{EQUATION OF PLANE: } 0.5985X - 0.2147Y - 0.7718Z = -1.6254^a$$

(B) ATOMS FORMING PLANE: Zr, S1, S1'

$$\text{EQUATION OF PLANE: } -0.0622X + 0.9978Y = 0.0$$

(C) ATOMS FORMING PLANE: S2, S3, C4, C5, C6, C7, C8, C9.

$$\text{EQUATION OF PLANE: } 0.6201X - 0.2685Y - 0.7372Z = -1.4221$$

DISTANCES OF ATOMS FROM PLANE (\AA);

S2	0.000(3)	C6	0.014(12)
S3	0.002(3)	C7	-0.013(14)
C4	-0.032(10)	C8	-0.016(15)
C5	-0.015(11)	C9	0.044(15)
Zr	-0.1303(8)		

(D) ATOMS FORMING PLANE: S2, S2', C1, C1', C2, C2', C3, C3'

$$\text{EQUATION OF PLANE: } -0.0717X + 0.9974Y = 0.0$$

DISTANCES OF ATOMS FROM PLANE (\AA):

S1	0.003(3)	C2	-0.046(13)
S1'	-0.003(3)	C2'	0.046(13)
C1	-0.016(10)	C3	0.044(15)
C1'	0.016(10)	C3'	-0.044(15)

(E) ATOMS FORMING PLANE: S1, S3', S2'

$$\text{EQUATION OF PLANE: } 0.9176X + 0.3961Y - 0.03372Z = -1.5424$$

Table 46 (continued)

^aX, Y, and Z are in Å and refer to the orthogonal coordinates along *a*, *b* and *c*^{*}.

TABLE 47: DIHEDRAL ANGLES BETWEEN
SELECTED PLANES

ATOMS IN PLANE 1	ATOMS IN PLANE 2	ANGLE (DEGREES)
(1) Zr, S2, S3	Zr, S2', S3'	101.1
(2) Zr, S2, S3	Zr, S1, S1'	104.7
(3) Zr, S2, S3	S2, S3, C4, C5, C6, C7, C8, C9	3.9
(4) Zr, S1, S1'	S1, S1', C1, C1', C2, C2', C3, C3'	0.5
(5) S2, S3, C4, C5, C6, C7, C8, C9	S2', S3', C4', C5', C6', C7', C8', C9'	95.0
(5) S2, S3, C4, C5, C6, C7, C8, C9	S1, S1', C1, C1', C2, C2', C3, C3'	108.2

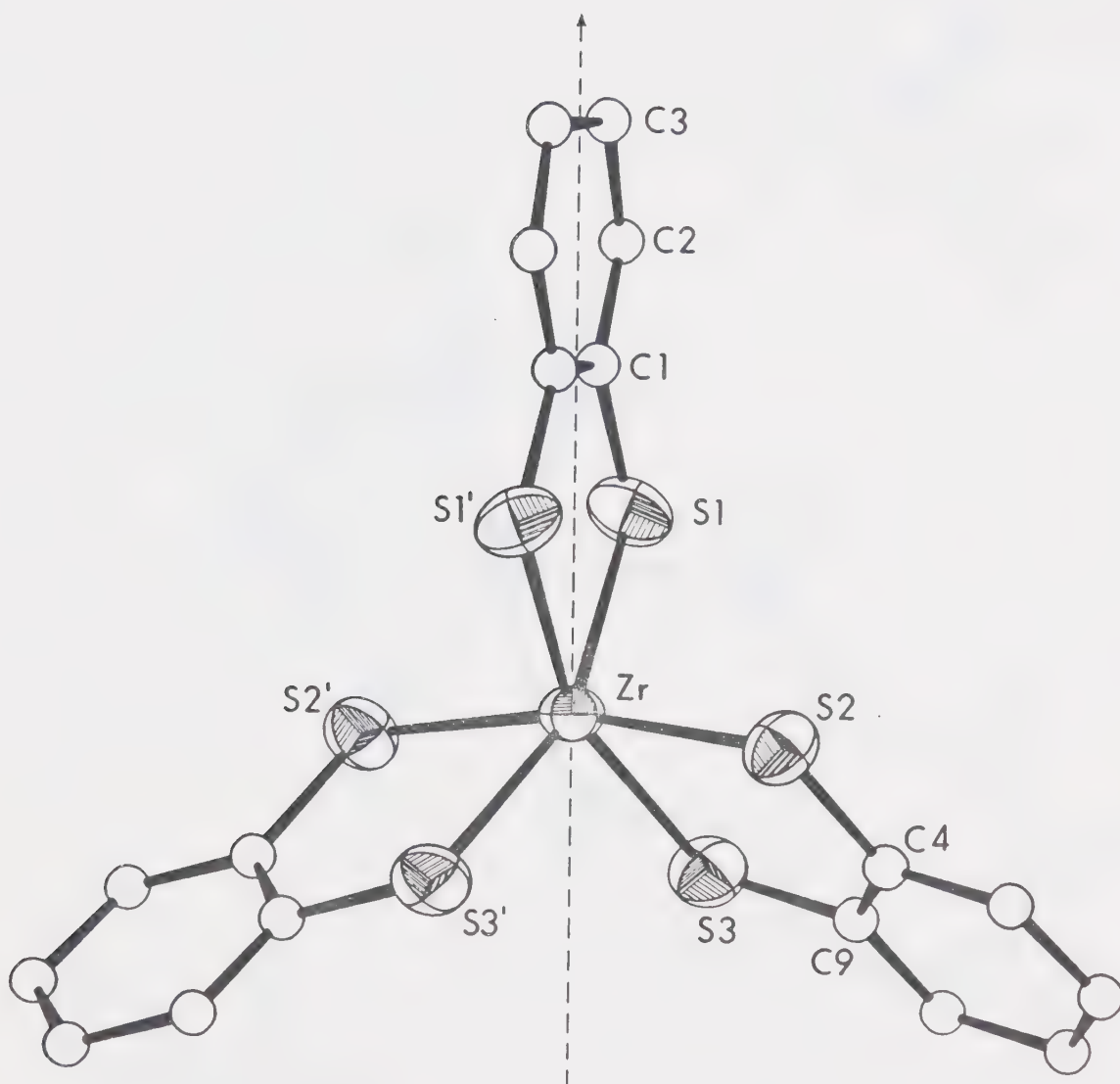


Fig. 17: A Perspective View of the $\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3^{2-}$ Dianion, Viewed Down the Approximate Molecular 3-Fold Axis.

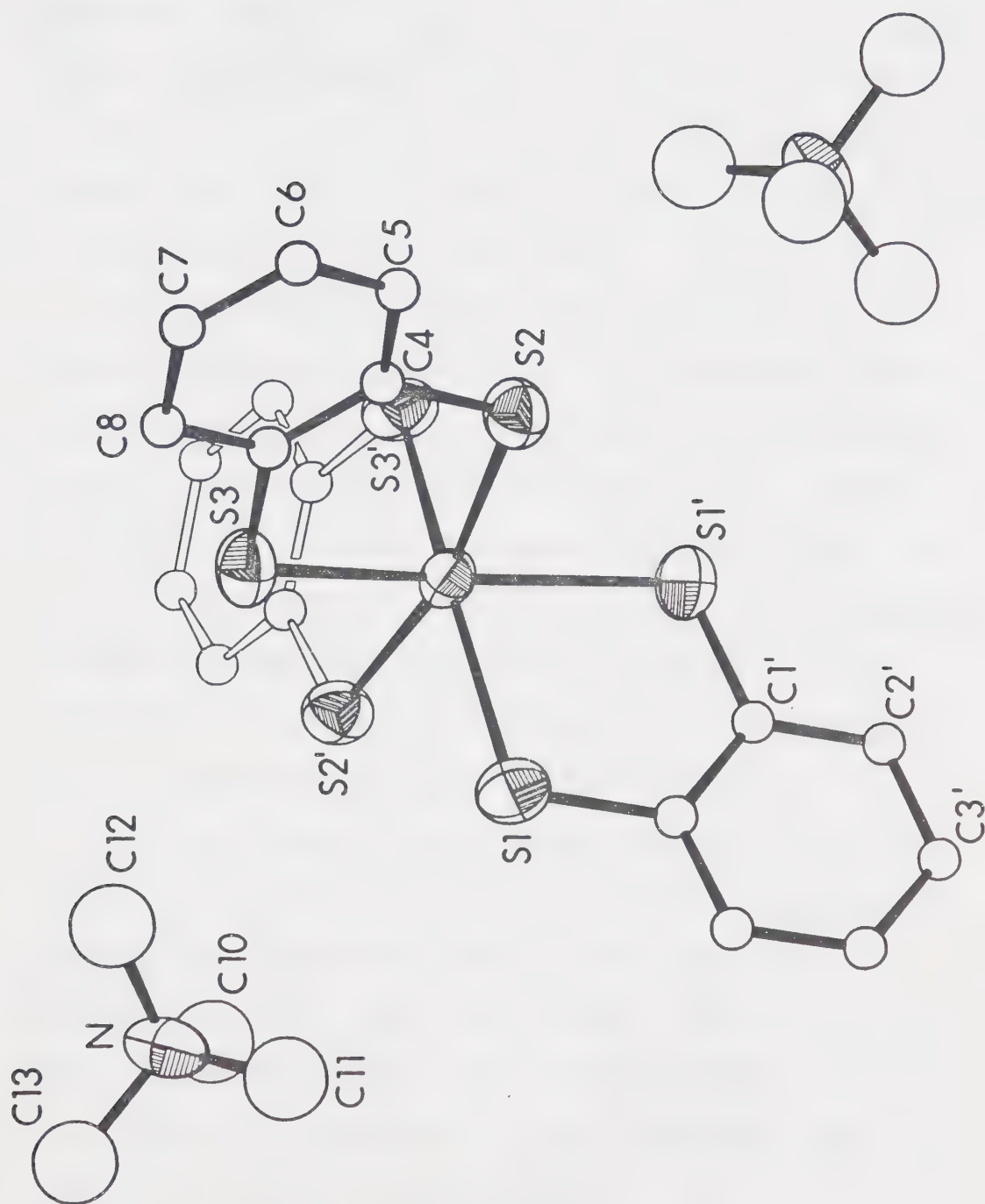


Fig. 18: A Perspective View of $[N(CH_3)_4]_2[Zr(S_2C_6H_4)_3]$

DESCRIPTION OF STRUCTURE

The $\text{Zr}(\text{bdt})_3^{2-}$ dianion, viewed down its approximate three-fold axis, is shown in Fig. 17, and the dianion and the two tetramethylammonium cations are shown in Fig. 18. The dianion is located on the crystallographic two-fold axis whereas the tetramethylammonium cations sit in general positions.

In the dianion, the six sulfur atoms are approximately equidistant from the zirconium atom and form a coordination polyhedron which is intermediate between an octahedron and a trigonal prism. Since the $\text{ZrS}_2\text{C}_6\text{H}_4$ fragments are approximately planar, the symmetry of $\text{Zr}(\text{bdt})_3^{2-}$ approximates D_3 . The dithiolene ligands radiate from the zirconium atom in a "propeller-like" arrangement as opposed to the "paddle-wheel" arrangement in the trigonal prisms.

In describing the degree of distortion of the metal coordination from either of the trigonal prismatic or octahedral limits, two parameters are especially useful; the S-M-S angles involving sulfur atoms which are almost *trans* to each other, and the projection angle between the two triangular faces of the prism (trigonal twist angle).

In a regular trigonal prism the S-M-S angle between pseudo '*trans*' sulfur atoms is approximately

136°. In an octahedron this angle is 180°. These two extremes are shown in Fig. 19, the S2-M-S4 angle being the angle of interest. However, for an

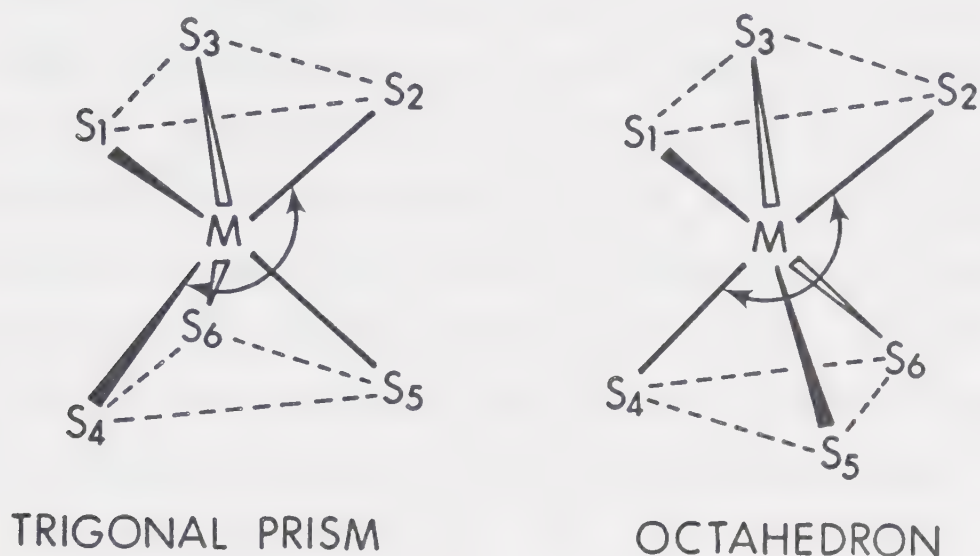


Fig. 19. *Trans* S-M-S Angles in the Trigonal Prism and the Octahedron.

intraligand S-Zr-S angle of $\sim 80^\circ$, considering only the geometric constraints of the ligand, a *trans* S-Zr-S angle of 170° is obtained as the corrected octahedral limit.¹⁶¹ The values observed for the $\text{Zr}(\text{bdt})_3^{2-}$ dianion [$167.76(8)^\circ$ and $159.80(7)^\circ$] are thus closer to the octahedral limit and on this basis the zirconium coordination can be described as distorted octahedral. The non-equivalence of these two independent values indicates that the distortion is not regular and that one ligand (containing S1 and S1') is

rotated more towards the trigonal prismatic structure than the other two ligands.

The other indication of the degree of distortion from the prismatic or octahedral limits is the trigonal twist or projection angle shown in Fig. 20. In the trigonal prism where the two triangular faces are eclipsed, this angle equals 0° , whereas in the ideal octahedron this angle is 60° . Again however, because of the constraint of ligand bite in these bidentate ligands, the octahedral limit is not attained. Rather, this angle will be limited by the ratio of intra-

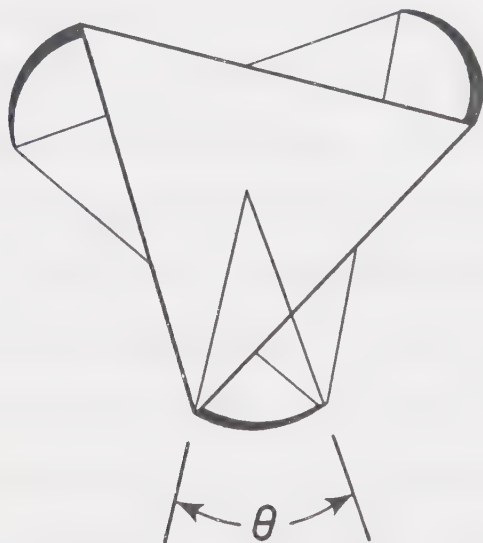


Fig. 20. Trigonal Twist Angle Projected Perpendicular to the Molecular 3-Fold Axis.

ligand S-S distances to the M-S distances. For the $\text{Zr}(\text{bdt})_3^{2-}$ dianion, this ratio (1.284) predicts¹⁶⁶ (on the basis of minimizing interligand repulsions) a twist angle of approximately 48° for the corrected octahedral limit. An average twist angle in this structure is calculated at 37° using equilateral triangles that correspond to a best fit with the observed individual atom coordinates. Thus the twist angle differs from the corrected octahedral limit by only 11° . By comparison, in the structure¹⁶⁷ of $\text{Al}(\text{O}_2\text{C}_7\text{H}_5)_3$, the observed trigonal twist angle (48.1°) is essentially that calculated using the constraints of ligand bite and this appears typical of structures where the only factor favouring the prism is minimization of the interligand repulsions. Thus the deviation of 11° from the corrected octahedral limit is significant and indicates a genuine tendency towards trigonal prismatic coordination in this structure.

The Zr-S distances (av. $2.543 \overset{\circ}{\text{\AA}}$) are longer than those observed in the molybdenum and niobium *tris* (benzene dithiol) complexes (see Table 48) and thus complete a trend through this series with the metal-sulfur distances increasing approximately as predicted by their covalent radii.¹³³ As with the niobium complex, the metal-sulfur distances again

contain irregularities of statistical significance. The Zr-S distance within the ligand bisected by the two-fold axis [$2.555(2) \text{ \AA}$] is longer than the other two independent Zr-S distances [$2.537(2) \text{ \AA}$ and $2.538(2) \text{ \AA}$].

Although this complex is of considerable interest in relation to the other *tris* dithiolenes, it is also interesting in its own right. The number of structurally characterized six coordinate zirconium complexes is small¹⁶⁸ and indeed $[\text{N}(\text{CH}_3)_4]_2[\text{Zr}(\text{bdt})_3]$ is believed to be the first example of a six coordinate zirconium-sulfur complex. The observed Zr-S distances lie midway between the values 2.49 \AA and 2.58 \AA , corresponding to the sums of the covalent and ionic (Zr^{4+} and S^{2-}) radii^{133,169} respectively.

The intraligand S-Zr-S angles (av. 79.77°) are slightly less than those observed in $\text{Mo}(\text{bdt})_3$ and $\text{Nb}(\text{bdt})_3^-$ (82.12° and 80.35° respectively) and complete a trend through the series. This trend is due to the relatively fixed ligand bite which does not increase as rapidly as the metal-sulfur distances.

The S-C distances seem to be an excellent indication of the tendency of the ligand towards either the oxidized or reduced formulations. In $\text{Zr}(\text{bdt})_3^{2-}$ the average S-C distance (1.765 \AA) is very close to

that predicted for a single bonded sulfur-carbon distance (1.77 \AA).^{84,133} Thus the ligand geometry approximates that corresponding to the dithiolato formulation and the formal oxidation state of (IV) appears to be a reasonable description for the zirconium atom in this structure. This structure is important in demonstrating that the ligand can attain the dithiolato limit. The carbon-carbon distances within the ligands (av. 1.384 \AA) are close to those observed in benzene.¹⁵⁸ However, as in the molybdenum and niobium complexes, shortening of the C_C-C_D bond is observed (see Fig. 21), probably due to thermal motion of the rings. In addition, in ligand 1, which is bisected by the crystallographic two-fold axis, the bond lengths vary significantly throughout the ring. One worrying feature of this ring is the presence of anomalously high thermal parameters (U_{11} 's) of the carbon atoms. This seems to indicate either a disorder or a systematic error is present. The disorder could correspond to the non-equivalence of Zr-S1 and Zr-S1' distances for a particular model. However, this problem is unlikely to affect the general conclusions of this study. The C-C bond lengths within the rings are therefore unreliable and no chemical significance should be placed on their

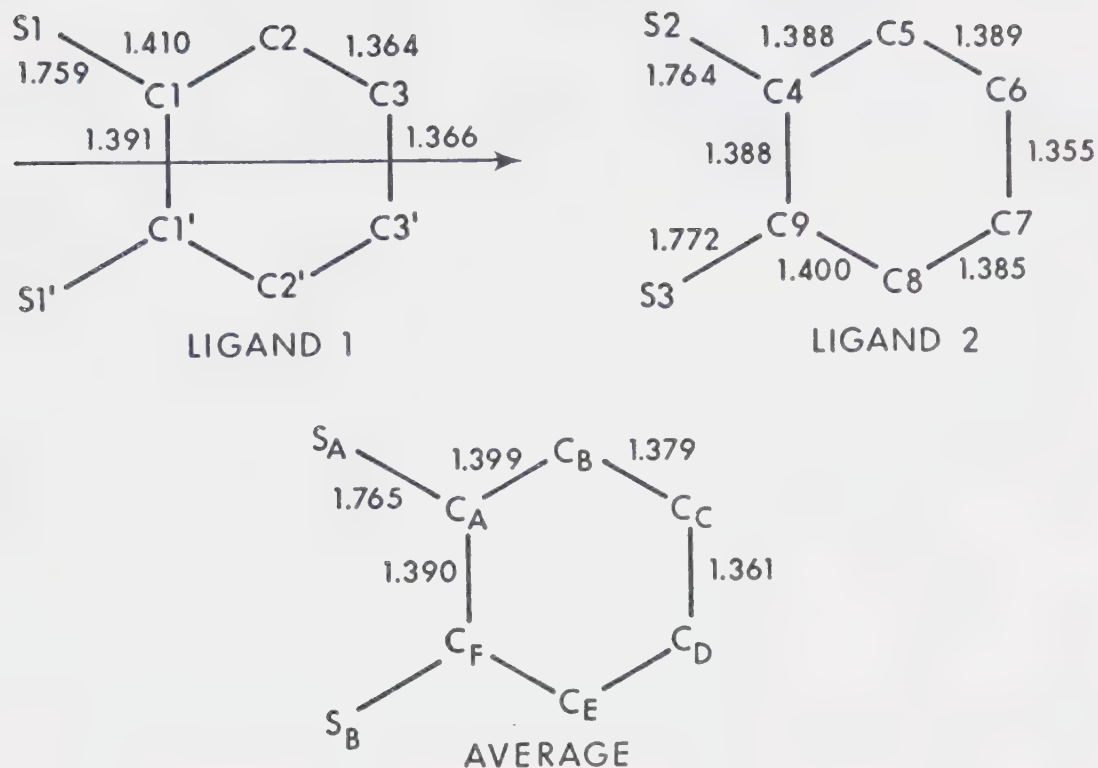


Fig. 21: Dimensions Within the Dithiolene Ligands.

differences.

The interligand S-S distances are, as expected, much longer than the intraligand distances, this due merely to the distortion towards the octahedron which maximizes the interligand separations. In addition the intraligand S-S distances in $\text{Zr}(\text{bdt})_3^{2-}$ are longer than those in $\text{Mo}(\text{bdt})_3$ and $\text{Nb}(\text{bdt})_3^-$, and are due to increasing S-C distances through the series. The

TABLE 48: SELECTED DISTANCES ($\overset{\circ}{\text{\AA}}$) FOR
FOR *TRIS*(1,2-DITHIOLENE) COMPLEXES

COMPOUND	M-S	S-S (INTRA)	S-S (INTER)	S-C	REFERENCE
$\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$	2.325(4)	3.032(10)	3.050(8)	1.69 ^a	129
$\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$	2.33(1)	3.10	3.11	1.70(3)	130
$\text{V}(\text{S}_2\text{C}_2\text{Ph}_2)_3$	2.338(4)	3.060(6)	3.065	1.69(1)	132
$\text{V}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$	2.36(1)	3.13(2)	3.20	1.72(2)	140
$\text{Mo}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$	2.373(4)	3.113	3.188	1.74(1)	141,170
$\text{W}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$	2.371(5)	3.112	3.193	1.73(2)	170
$\text{Fe}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{2-}$	2.261(2)	3.147(2)	3.19	1.731(4)	142
$\text{In}[\text{S}_2\text{C}_2(\text{CN})_2]_3^{3-}$	2.604(8)	3.40(1)	3.89(1)	1.72(3)	171
$\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$	2.367(2)	3.110(3)	3.091(2)	1.727(6)	THIS WORK
$\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3^-$	2.441(2)	3.150(3)	3.232(3)	1.744(7)	"
$\text{Zr}(\text{S}_2\text{C}_6\text{H}_4)_3^{2-}$	2.543(2)	3.265(3)	3.584(2)	1.765(6)	"

^aWhere standard deviations are not shown, they were not given in the original paper. In $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ the standard deviations are not shown due to a wide range in S-C distances.

TABLE 49: SELECTED ANGLES FOR TRIS (1,2-DITHIOLENE) COMPLEXES (DEGREES)

COMPOUND ^d	S-M-S (INTRA)	S-M-S (TRANS)	PROJECTION ANGLE ^c	DIHEDRAL MS ₂ /LIGAND ANGLE	COORDIN- ATION
Re(S ₂ C ₂ Ph ₂) ₃	81.4(4)	~136	<1	--	TRIGONAL PRISM
Mo(S ₂ C ₂ H ₂) ₃	82.5	~136	0	18	"
V(S ₂ C ₂ Ph ₂) ₃	81.7(2)	~136	8.5 ^a	--	"
V[S ₂ C ₂ (CN) ₂] ₃ ²⁻	--	158.6	TWISTED ^b	--	DISTORTED OCTAHEDRON
Mo[S ₂ C ₂ (CN) ₂] ₃ ²⁻	82.3(2)	156	28	~2	"
W[S ₂ C ₂ (CN) ₂] ₃ ²⁻	82.1(2)	156	28	~2	"
Fe[S ₂ C ₂ (CN) ₂] ₃ ²⁻	88.0(1)	--	~60	--	OCTAHEDRON
In[S ₂ C ₂ (CN) ₂] ₃ ³⁻	81.5(3)	169.3(3)	--	--	DISTORTED OCTAHEDRON
Mo(S ₂ C ₆ H ₄) ₃	82.18(8)	135.70(7)	0	13.1, 21.1, 30, 0	TRIGONAL PRISM
Nb(S ₂ C ₆ H ₄) ₃ ⁻	80.35(7)	135.06(7)	0.7	22.4	TRIGONAL PRISM
Zr(S ₂ C ₆ H ₄) ₃ ²⁻	79.77(7)	163.78(8)	37.0	3.9, 0.5	DISTORTED OCTAHEDRON

^aCalculated in ref. 172 from atomic coordinates given in original paper.^bNo coordinates or twist angle given.^cTrigonal twist angle projected perpendicular to molecular 3-fold axis.^dReferences shown in Table 48.

S-C-C and C-C-C angles within the ligands are all close to the expected value of 120° .

An interesting feature observed in $\text{Mo}(\text{bdt})_3$ and isoelectronic $\text{Nb}(\text{bdt})_3^-$ is the large bend of the MS_2 planes from the ligand S_2C_6 planes (21.4° and 22.4° respectively). This had also been observed in $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ ¹³⁰ and $\text{Mo}[\text{Se}_2\text{C}_2(\text{CF}_3)_2]_3$ ¹⁵² but was not observed in $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ ¹²⁹ or $\text{V}(\text{S}_2\text{C}_2\text{Ph}_2)_3$ ¹³². In $\text{Zr}(\text{bdt})_3^{2-}$ these planes are approximately coplanar, the dihedral angles between ZrS_2 and S_2C_6 planes being 3.9° and 0.5° . Although Schrauzer had attributed¹³⁸ the bend observed in $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$ as due to hybridization of the sulfur atoms between sp^2 and sp^3 , it is then difficult to account for the near planarity of the ligands in the zirconium, rhenium and vanadium complexes.

Comparison of the angular parameters in Table 49 allows the complexes to be placed in order of increasing tendency toward the trigonal prismatic structure. Consideration must be given to the general criticism of X-ray crystallographic studies, that one cannot guarantee that the observed geometry corresponds to the ground state. Thus the differences between $\text{V}(\text{mnt})_3^{2-}$ and $\text{Mo}(\text{mnt})_3^{2-}$ [or $\text{W}(\text{mnt})_3^{2-}$] may not be significant. The order for the dianionic species is then:

corrected
octahedral \simeq Fe(mnt) $_3^{2-}$ < Zr(bdt) $_3^{2-}$ <
limit

V(mnt) $_3^{2-}$
Mo(mnt) $_3^{2-}$ << trigonal
prismatic
limit
W(mnt) $_3^{2-}$

The corresponding order for the isoelectronic series,
as described in this thesis is:

corrected
octahedral < Zr(bdt) $_3^{2-}$ << Nb(bdt) $_3^-$ \leq Mo(bdt) $_3$
limit

trigonal
= prismatic
limit.

Chapter IX presents a general rationalization for
these trends.

A perspective view of the dianion and the tetra-
methyammonium cations is shown in Fig. 18. As
expected the cations are close to tetrahedral, with
the small distortions present being due to packing
effects. The average N-C distance (1.474 Å) agrees
quite well with that predicted (1.47 Å) assuming
single bonded covalent radii.¹³³ This value is also
in good agreement with previous structural determina-
tions in which the tetramethylammonium cation was
involved.^{173,174}

CHAPTER IX: TRIGONAL PRISMATIC *vs.* OCTAHEDRAL
COORDINATION IN *TRIS* (1,2-DITHIOLATO) COMPLEXES

The isoelectronic series of *tris* (1,2-dithiolato) complexes, described in the latter part of this thesis, show dramatic changes in the coordination polyhedron. These changes, from an almost perfect trigonal prism in the neutral molybdenum complex, to a very slightly distorted trigonal prism in the niobium complex anion, to a distorted octahedron in the zirconium complex dianion, are accompanied by smooth increases in metal-sulfur distances, sulfur-carbon distances, and interligand sulfur-sulfur distances (see Table 48). These changes correspond to the increasing importance of the dithiolato formulation for the ligand, that is, $S_2C_6H_4^{2-}$. The increase in interligand sulfur-sulfur distances would lead to a reduction in direct sulfur-sulfur bonding, which has been postulated as a factor in stabilizing the prism.^{137,138,170} In this chapter the structural trends are correlated with molecular orbital energy level diagrams.

Two energy level schemes have been presented to account for the stability of the prism in certain *tris* (1,2-dithiolato) complexes. One of these schemes, due to Schrauzer and Mayweg¹³⁸ (which will be referred to as scheme 1) is presented for an unspecified first

METAL

LIGAND

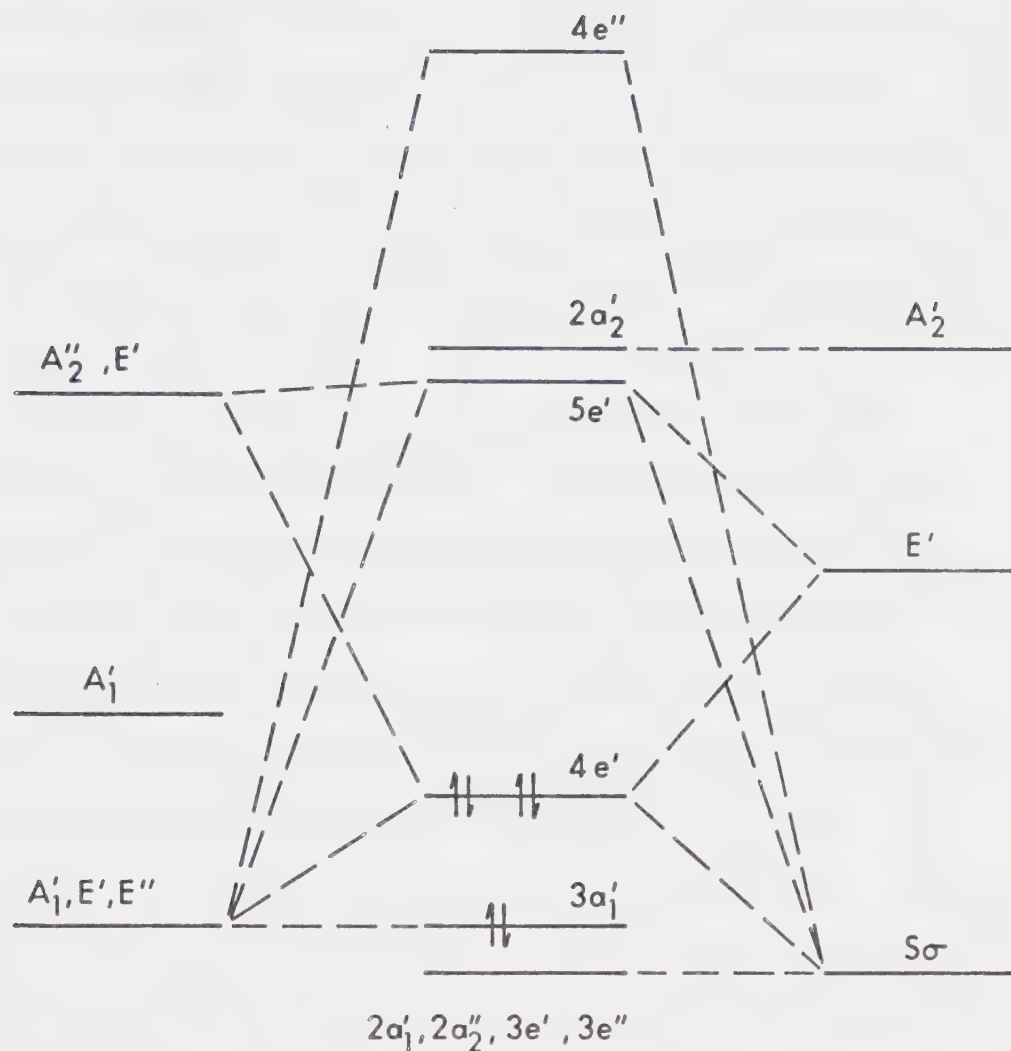


FIG. 22: MOLECULAR ORBITAL ENERGY LEVELS OF INTEREST FOR TRIGONAL PRISMATIC DITHIOLENES, BY G. N. SCHRAUZER AND V. P. MAYWEG

transition series element. The important levels of this scheme are shown in Fig. 22. The alternative scheme, due to Gray *et. al.*¹³⁷ (which will be referred to as scheme 2), is shown in Fig. 23. The differences between the two schemes arise, in part, from the relative positions of the metal and ligand orbitals.¹³² Both schemes agree on the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} orbitals with appropriate combinations of ligand π orbitals (symmetry b_1 for an isolated ligand) to give bonding $4e'$ and antibonding $5e'$ levels. Scheme 2, however, proposes an additional significant interaction between the metal d_{z^2} orbital and ligand non-bonding sigma orbitals, giving one bonding ($2a_1'$) and one antibonding ($3a_1'$) level. Scheme 1 has also been challenged on the basis of electron spin resonance studies,^{132,175} and can be shown to be inconsistent with the electronic spectra in this series of compounds. Specifically it predicts an increase in the frequency that would correspond to the transitions $3a_1' \rightarrow 5e''$ and $3a_1' \rightarrow 2a_2'$ when comparing the niobium complex with the molybdenum complex, which is the opposite of the experimental results (Table 18). Scheme 2 correctly predicts the experimental observations, as Gray *et. al.*¹³⁷ attribute the transitions as due to $2a_2''(\pi_h)$, $3e'(\pi_h) \rightarrow 3a_1'(d_{z^2})$.

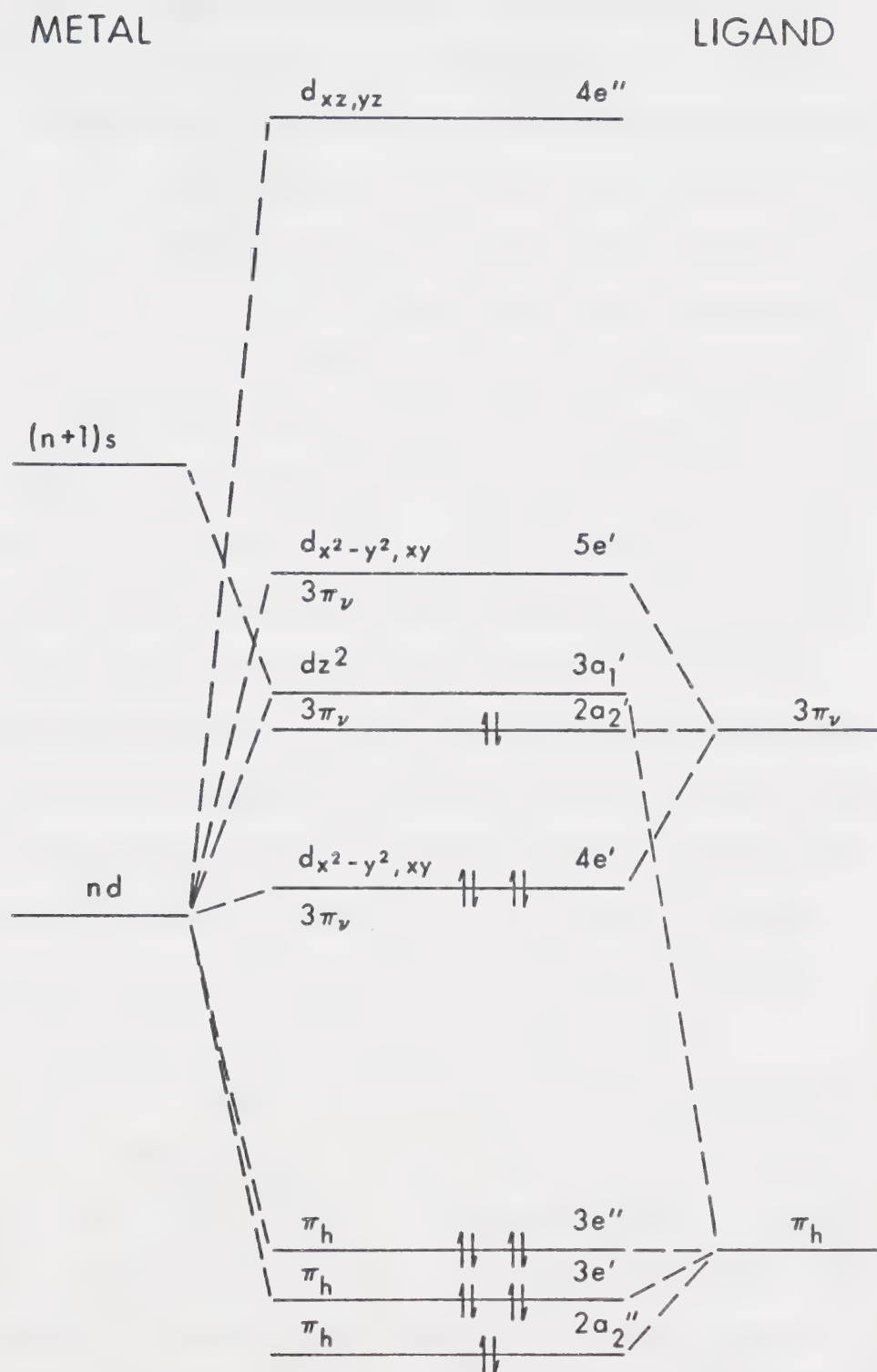


FIG. 23: MOLECULAR ORBITAL ENERGY LEVELS OF INTEREST FOR TRIGONAL PRISMATIC DITHIOLENES, BY H. B. GRAY *et. al.*

Since scheme 2 seems more consistent with the experimental results, it is favoured over scheme 1, and therefore will be used in all subsequent discussions. In this M.O. description (Fig. 23), the levels $2a_2''$, $3e'$ and $3e''$ consist mainly of sulfur sp^2 hybrid orbitals (π_h) at 120° to the σ orbitals pointing at the metal. The $2a_2'$ orbital is non-bonding and the $3a_1'$ is principally metal in character, having symmetry d_{z^2} . The $4e'$ and $5e'$ are both metal ($d_{x^2-y^2}, d_{xy}$) and ligand ($3\pi_v$) in character and both are strongly delocalized over the metal and ligands. Stability of the prism was postulated, by Gray *et. al.* as due to interaction of the sulfur π_h orbitals with the metal d_{z^2} orbital producing the stable bonding orbital $2a_1'$, which is always filled; also the interaction of the metal $d_{x^2-y^2}$ and d_{xy} orbitals with the $3\pi_v$ ligand orbitals produces the stable $4e'$ orbitals which are also filled in these complexes.

In order to use the M.O. scheme by Gray *et. al.* it must be shown that it will apply to the series of interest in this thesis. Considering the ligand and metal orbitals separately, it can first be shown that the energy levels of the molybdenum 4d and rhenium 5d orbitals are similar.¹⁷⁶ Therefore use of the molybdenum atom instead of rhenium in scheme 2 is justified.

The energy levels of the ligands $S_2C_2H_2$ and $S_2C_6H_4$ can be compared using the calculations of Birss and Das Gupta.¹⁶⁰ The π orbitals for these ligands, the calculated orbital energies and geometries are presented in Figs. 24, 25 and 26. Each ligand is shown in the reduced form (corresponding to the dithiolato limit) and in the neutral or oxidized form (2π electrons less). The π orbitals of particular interest are the $2b_1$ for $S_2C_2H_2$ and $3b_1$ for $S_2C_6H_4$. Comparing the oxidized forms of the ligands, the energies of the $2b_1$ ($S_2C_6H_2$) and $3b_1$ ($S_2C_6H_4$) levels are -16.4 e.v. and -15.3 e.v. respectively. A comparison of the reduced forms of the ligands shows the energies are -10.2 e.v. and -10.0 e.v. for the same levels. The probable error in these energy levels is of the order of 0.3 e.v.. Thus it is clear that the molecular orbital scheme proposed for $Re(S_2C_2H_2)_3$ should closely approximate that used for $Mo(S_2C_6H_4)_3$, because of the near equality of both metal and ligand orbital energies.

As postulated by Gray *et. al.*,¹³⁷ the stability of the prism is due, in part, to the interaction of the ligand $3\pi_v$ and metal $d_{x^2-y^2}$ and d_{xy} orbitals, producing the $4e'$ orbital. The series, $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$, permits examination of this

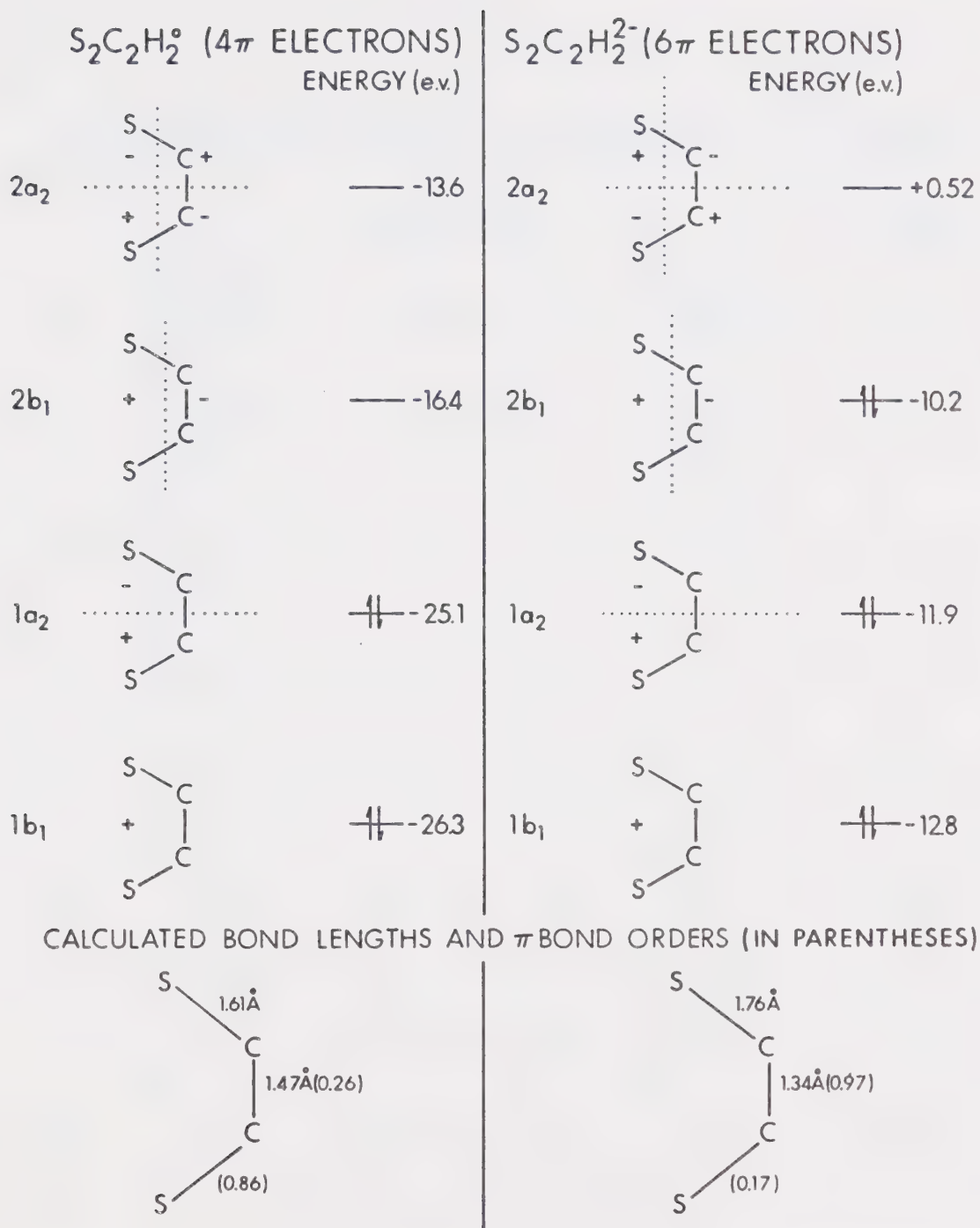


FIG. 24: REPRESENTATIONS OF THE MOLECULAR ORBITALS
AND ENERGY LEVELS FOR $S_2C_2H_2$ AND $S_2C_2H_2^{2-}$

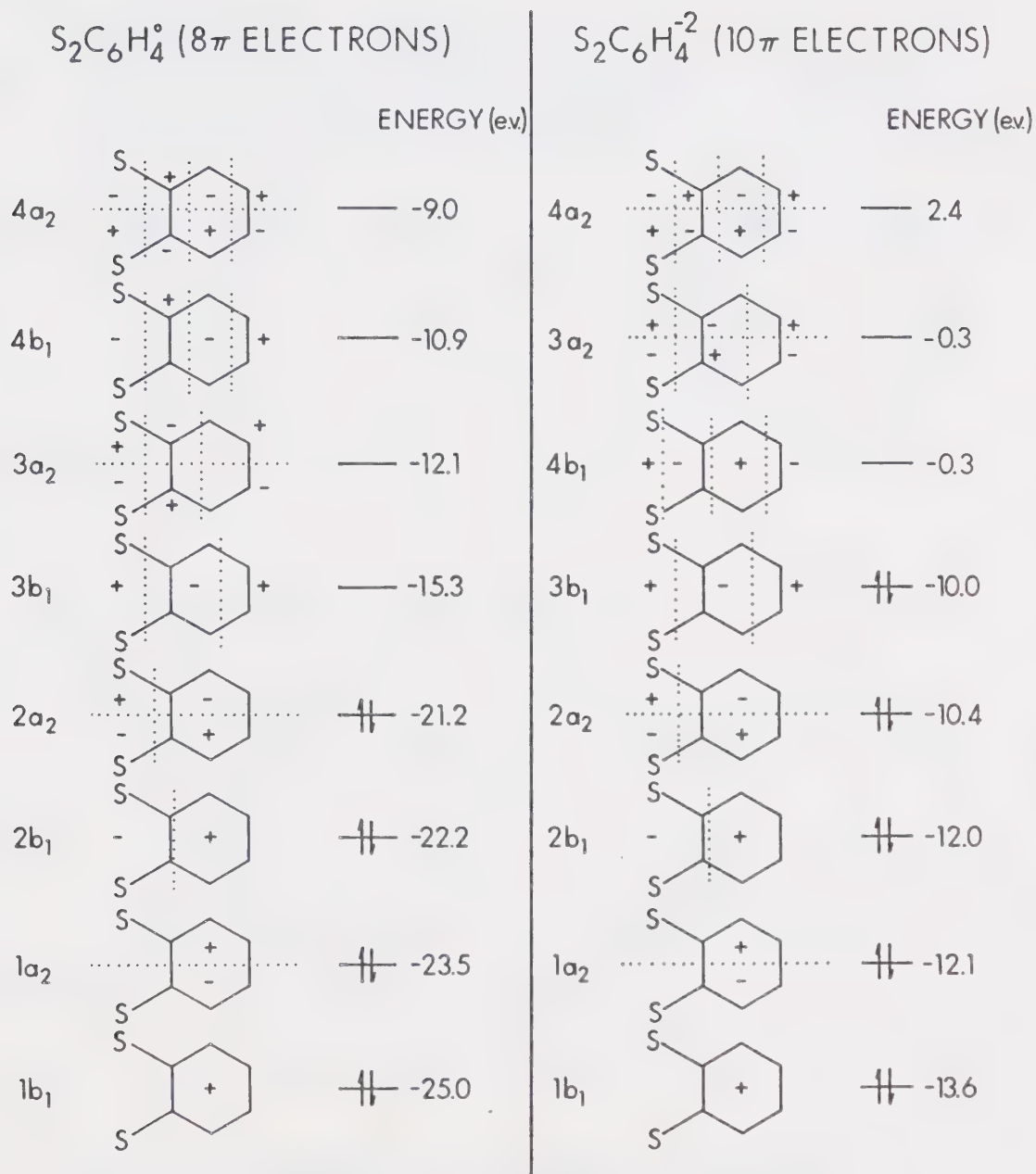


FIG. 25: REPRESENTATIONS OF THE MOLECULAR ORBITALS
AND ENERGY LEVELS FOR $S_2C_6H_4$ AND $S_2C_6H_4^{2-}$

A. CALCULATED BOND LENGTHS

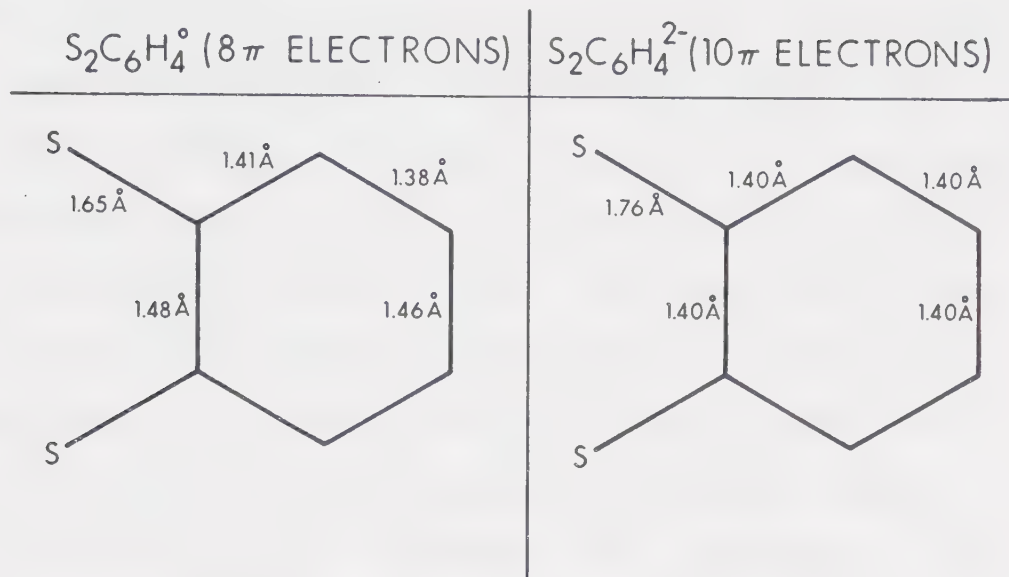
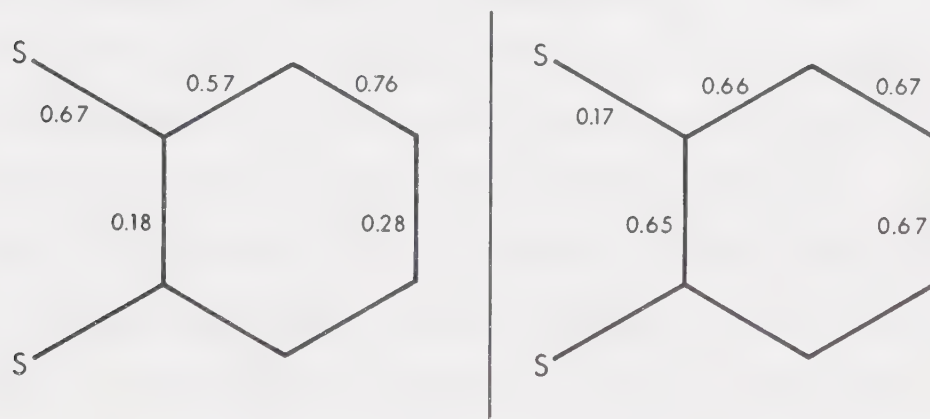
B. CALCULATED π BOND ORDERS

FIG. 26: PREDICTED BOND LENGTHS AND π BOND ORDERS FOR $S_2C_6H_4$ AND $S_2C_6H_4^{2-}$

postulate, since in this isoelectronic series no change in the geometry of the coordination polyhedra can be attributed to the occupation of the antibonding orbitals, as has been postulated^{141,170} for the destabilization of the prisms in $\text{Mo}(\text{mnt})_3^{2-}$ and $\text{W}(\text{mnt})_3^{2-}$.

The $4e'$ level should be extremely sensitive to the metal d orbital energies due to the near-equivalence in energy of the d orbitals and the $4e'$ level. The $2a'_1$ level will also be affected but not as much, due to the greater energy separation of it from the metal d orbitals. As the d orbital energies increase, the $4e'$ level should be destabilized and should become more ligand ($3\pi_v$) in character. This increase in the ligand character of the $4e'$ level should be paralleled by a structural change, corresponding to an increase in the contribution of the reduced form structure. The molecular orbital description of the ligands is used in preference to the oversimplified valence bond descriptions, that is, the dithiolato and dithioketonic structures, shown in Fig. 11, since the discussion concerns energy levels and not just geometric changes.

The ligand undergoes extensive geometric changes upon the reduction:



as is shown in Fig. 26. In principle, both sulfur-carbon and carbon-carbon distances could be used in assessing the relative importance of the reduced and oxidized structures in a particular case. In practice, the high uncertainty in the carbon-carbon bond lengths (due to naturally higher standard deviations and large effects due to thermal motion) makes them unsuitable for a semi-quantitative discussion and the more reliable sulfur-carbon distances provide the only useful guide. Sulfur-carbon bond lengths for the *tris* (benzene-1,2-dithiolato) complexes, described in this thesis, and the theoretical geometries of the oxidized and reduced formulations can be ordered as follows:

$$\text{S}_2\text{C}_6\text{H}_4^{\circ}, (1.648 \text{ \AA}) < \text{Mo}(\text{bdt})_3, (1.727 \text{ \AA}) < \\ \text{Nb}(\text{bdt})_3^-, (1.744 \text{ \AA}) < \text{Zr}(\text{bdt})_3^{2-}, (1.765 \text{ \AA}) \approx \text{S}_2\text{C}_6\text{H}_4^{2-}, \\ (1.763 \text{ \AA}).$$

This series indicates that the ligand tends toward the reduced geometry as the energy of the d orbital increases.

In assessing the ligand and metal orbital character of the $4e'$ level, it should be noted that appropriate extremes do not correspond to $[\text{S}_6\text{C}_{18}\text{H}_{12}]^{\circ}$ and $[\text{S}_6\text{C}_{18}\text{H}_{12}]^{6-}$ (equivalent to three ligands in the oxidized and reduced forms), since the ligand $3\pi_v$ orbitals give rise to the $2a'_2$ level as well as the $4e'$ level (see Fig. 23). This $2a'_2$ level is non-bonding,

entirely located on the ligand and is always occupied by two electrons. Hence the discussion of the $4e'$ levels must utilize limiting geometries defined by $[S_6C_{18}H_{12}]^{2-}$ and $[S_6C_{18}H_{12}]^{6-}$, that is, allowing for the $2a'_2$ occupancy.

Fig. 27 shows the plots of S-C bond length *vs.* S-C π bond order for the ethylene and benzene dithiol ligands, as calculated by Birss and Das Gupta.¹⁶⁰ The limiting extremes, $S_2C_2H_2$ and $S_2C_2H_2^{2-}$, also $S_2C_6H_4$ and $S_2C_6H_4^{2-}$, are shown on the respective plots. For the ligand system $S_6C_{18}H_{12}^{2-}$, the π bond order and bond length can be calculated assuming one contribution of $S_2C_6H_4^{2-}$ for two contributions of $S_2C_6H_4$. This yields a S-C π bond order of 0.50 and a corresponding S-C bond length of 1.69 \AA . If the $4e'$ levels are completely ligand in character, the ligand $3\pi_v$ orbitals would contain 6 electrons and would be described as $S_6C_{18}H_{12}^{6-}$. The S-C π bond order and S-C bond length for this extreme are 0.17 and 1.76 \AA respectively. These two limits, $S_6C_{18}H_{12}^{2-}$ and $S_6C_{18}H_{12}^{6-}$, then correspond to the extremes that the $4e'$ orbital is completely metal and completely ligand in character, respectively.

In $Mo(bdt)_3$ the average S-C bond length (1.727 \AA) corresponds to a π bond order of 0.32 and thus lies

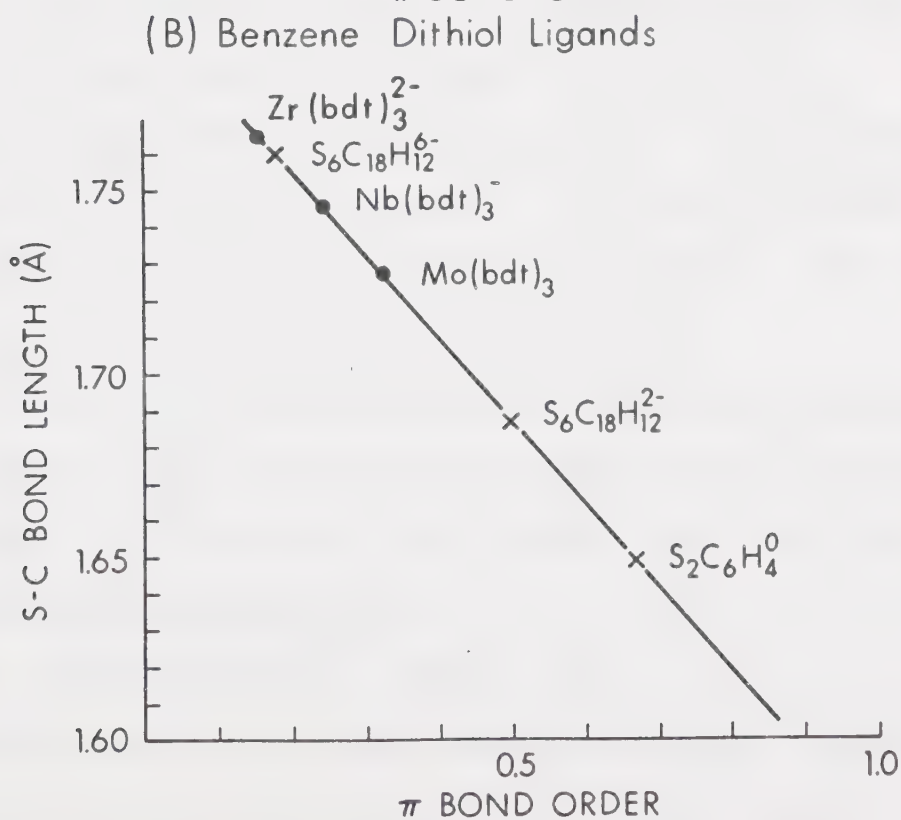
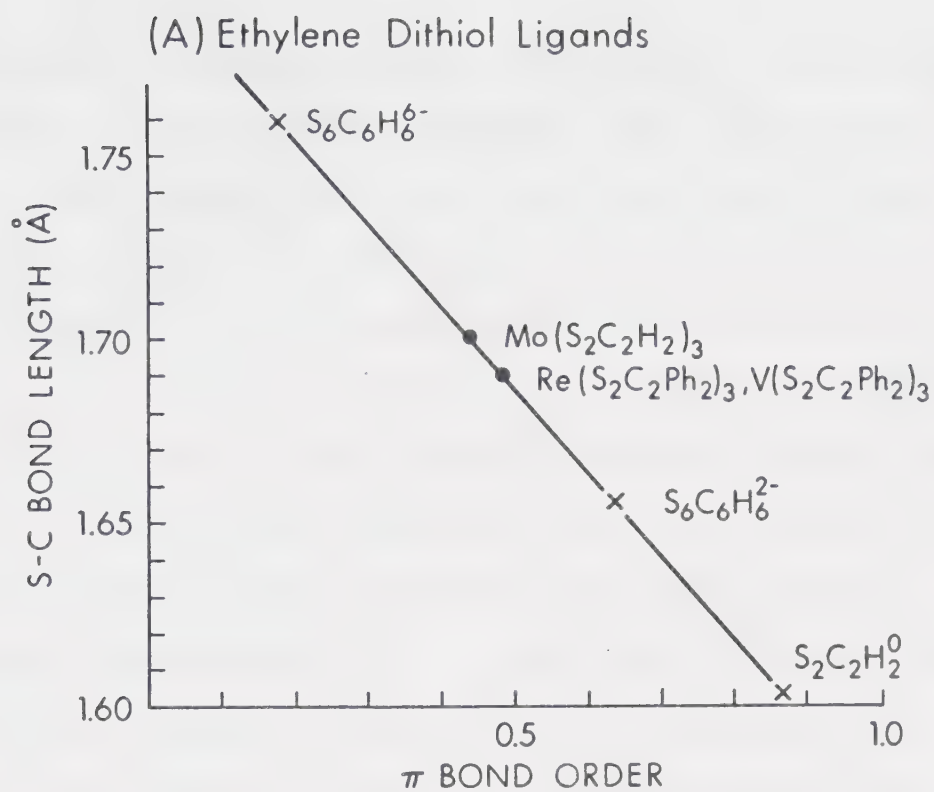


FIG. 27: S-C BOND LENGTH *vs.* π BOND ORDER FOR ETHYLENE AND BENZENE DITHIOL LIGANDS

approximately midway between the $S_6C_{18}H_{12}^{6-}$ and $S_6C_{18}H_{12}^{2-}$ extremes. The $4e'$ level therefore has approximately equal contributions from the metal and ligand orbitals. In $Nb(bdt)_3^-$ the S-C bond length of 1.744 \AA and π bond order of 0.24 corresponds to three quarters of the electron density of $4e'$ being on the ligand and only one quarter of the electron density being on the metal. The S-C bond length of 1.765 \AA in $Zr(bdt)_3^{2-}$ indicates that the ligand has reached the limiting reduced formulation. It is to be noted, however, that there is a tendency in the zirconium coordination toward the trigonal prism, indicating possibly that the $4e'$ level still has a small amount of metal contribution. It is also possible that the tendency toward the prism is favoured by the overlap of the ligand π_h and metal d_{z^2} orbitals, which may still be operative.

In Chapter V it was mentioned that any comparison in bond lengths between ethylene and benzene dithiol ligands should be made with extreme care. This can now be demonstrated with the aid of the calculations by Birss and Das Gupta,¹⁶⁰ shown in Fig. 27. In the ethylene dithiol ligands, employing similar arguments as used for the benzene dithiol ligands, the S-C bond lengths and π bond orders can be calculated for

the $S_6C_6H_6^{2-}$ and $S_6C_6H_6^{6-}$ extremes. These bond lengths and π bond orders are 1.66 Å and 0.64 for $S_6C_6H_6^{2-}$ and 1.76 Å and 0.17 for $S_6C_6H_6^{6-}$. Thus although $Mo(S_2C_2H_2)_3$ has S-C distances (av. 1.70 Å) which are shorter than in $Mo(bdt)_3$, a comparison on Fig. 27 shows that in the two complexes the 4e' level has a similar make-up. It is therefore apparent that for different ligands, even in similar bonding situations, differences in bond lengths are to be expected.

The series of complexes, $Mo(bdt)_3$, $Nb(bdt)_3^-$ and $Zr(bdt)_3^{2-}$ therefore shows the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} with the ligand π_v orbitals in stabilizing the trigonal prism. In addition, the prism stability in this series is maximized in $Mo(bdt)_3$, where the 4e' orbital contains approximately equal contributions from metal and ligand and thus the electrons are completely delocalized over the metal-ligand framework. In the 1,1-dithiolato complexes¹⁷⁷⁻¹⁸⁴ the ligands do not have orbitals of the proper symmetry and energy to overlap with the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal.¹⁵⁷ Therefore this delocalization is not possible and all 1,1-dithiolato complexes have distorted octahedral coordinations.

Interligand sulfur-sulfur bonding has also been

presented as a reason for prism stability,^{137,138,170} and the trends observed in the benzene dithiol series can also be explained by assuming that a breakdown in S-S bonding occurs, progressing from the molybdenum complex through to the zirconium complex. As the d energies increase, so also do the metal radii. Therefore, as the metal radii increase from Mo to Nb to Zr, the interligand S-S distances increase and the slight distortion observed in $\text{Nb}(\text{bdt})_3^-$ can be explained as a partial breakdown in this S-S bonding. At $\text{Zr}(\text{bdt})_3$ presumably the sulfur atoms have been forced far enough apart to result in a distorted octahedral coordination, due to an almost complete breakdown in S-S bonding. A significant argument, however, against sulfur-sulfur bonding as a major stabilizing force in the prism can be seen in a comparison of $\text{Mo}(\text{mnt})_3^{2-}$ and $\text{W}(\text{mnt})_3^{2-}$ with $\text{Nb}(\text{bdt})_3^-$. In the niobium complex the interligand sulfur-sulfur distances are greater than those in the molybdenum or the tungsten dianions (see Table 48), yet the niobium complex is trigonal prismatic, whereas the dianions are distorted octahedrons.

The major argument for sulfur-sulfur bonding has been the short sulfur-sulfur contacts observed in the prisms, as compared with the predicted van der Waals

contacts¹⁵¹ (3.70 Å). However these contacts probably arise as a consequence of other factors which stabilize the prism, and are probably not themselves the reason for this geometry. It is believed that the forces between the sulfur atoms are repulsive in nature rather than attractive, as proposed.^{137,138,170} This can offer a possible explanation for the geometry observed¹³² in $V(S_2C_2Ph_2)_3$, which is distorted slightly from the prism by a trigonal twist of 8.5°. If, as suspected, the prism dimensions in the rhenium and molybdenum complexes^{129,130} have reached their minimum, due to increasing S-S repulsions, then in the vanadium complex the smaller size of the metal could result in poor overlap of the metal and ligand orbitals (possibly ligand π_h with metal d_{z^2}). It is then possible that in order to attain the maximum stability, the prism distorts slightly by the observed trigonal twist. In this respect a complete structural determination of $Cr(S_2C_2Ph_2)_3$ is desirable, since X-ray power photographs indicated^{128,129} it is isomorphous with $V(S_2C_2Ph_2)_3$. However, since the chromium radius is smaller than that of vanadium,¹³³ if the above arguments apply, the coordination of the chromium complex should be more distorted from the prism than the vanadium complex.

Any proposed sulfur-sulfur bonding can occur by two mechanisms: overlap of the sulfur p orbitals perpendicular to the ligand plane (π_v orbitals), or overlap of the non-bonding sulfur lone pair (π_h orbitals). It is not believed, however, that either mechanism has a significant effect in stabilizing the prism, since both types of overlap are possible in the 1,1-dithiolato systems, yet these systems invariably have geometries which are close to the "corrected" octahedral limit.

In conclusion, the importance of the $4e'$ molecular orbital in stabilizing the trigonal prism is evidenced in the series: $\text{Mo}(\text{bdt})_3$, $\text{Nb}(\text{bdt})_3^-$ and $\text{Zr}(\text{bdt})_3^{2-}$. The increasing energies of the metal d orbitals, progressing from the molybdenum to the zirconium complex, destabilizes the $4e'$ level, which in turn results in destabilization of the prism. Interligand sulfur-sulfur bonding is not believed to be a significant factor in stabilizing the prism.

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APPENDIX 1: MOLECULAR DISORDER IN TETRACARBONYL  
RHENIUM BIS ( $\mu$ -DIPHENYLSILICON)

RHENIUM TETRACARBONYL,  $[\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2]$ .

The crystal and molecular structure of  $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$  was solved by X-ray diffraction techniques by Bennett and Haas.<sup>64</sup> The compound crystallizes in the monoclinic space group  $C2/m$  with two discrete molecules per unit cell, thus imposing site symmetry  $2/m$  on the molecule. The unit cell dimensions are:  $a = 13.976(3) \text{ \AA}$ ,  $b = 10.549(1) \text{ \AA}$ ,  $c = 12.025(3) \text{ \AA}$ ,  $\beta = 117.57(6)^\circ$ , giving an observed density  $1.98(2) \text{ g cm}^{-3}$ , which agrees well with the calculated value of  $2.03 \text{ g cm}^{-3}$ . A three dimensional representation of the molecule is shown in Fig. 28. The molecule bears a strong resemblance to the related hydrides  $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$  and  $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ , having an almost identical  $\text{Re}_2\text{Si}_2$  framework. As in the hydrides, two mutually *trans* carbonyl groups on each rhenium atom are perpendicular to the  $\text{Re}_2\text{Si}_2$  plane. The other carbonyl groups are approximately *trans* to the Re-Si bonds.

The crystals contain discrete and disordered molecules, the disorder involving the phenyl groups attached to each silicon atom. One phenyl ring is located approximately in the crystallographic mirror and the other lies approximately perpendicular





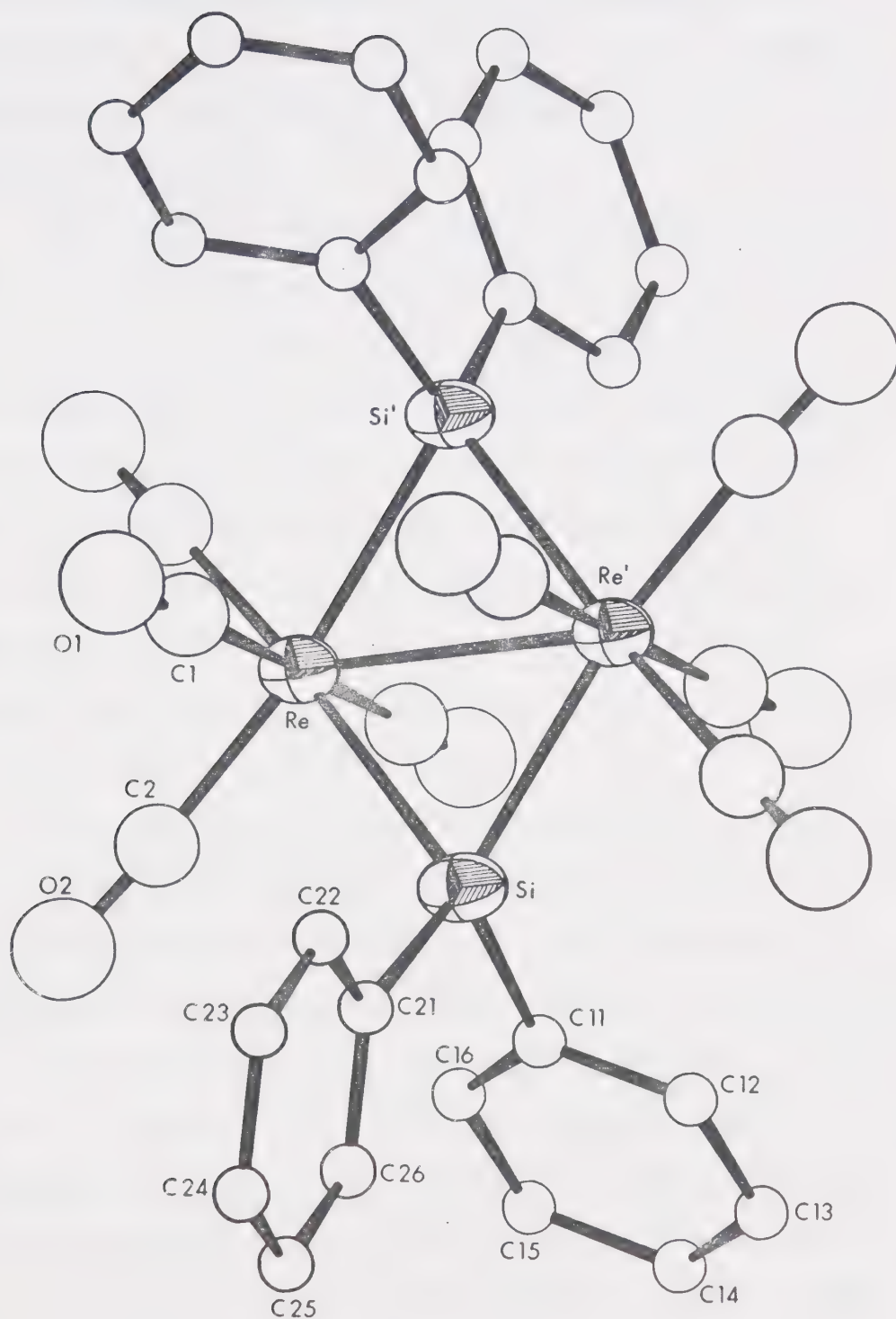


FIG. 28: A PERSPECTIVE VIEW OF  $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$



to it. Final refinement of this disordered model yielded  $R_1 = 0.036$  and  $R_2 = 0.057$  for 1153 independent reflections refining 52 parameters in the least squares refinement.

The final anisotropic thermal parameters ( $U_{ij}$ 's) for Re and Si are shown in Table 50, and the final positional parameters and the isotropic B's are shown in Table 51. Bond lengths and angles along with their standard deviations are shown in Table 52. In the representation of the molecule (Fig. 28) only one pair of disordered phenyl groups are shown for clarity. In addition the ring carbon atoms are given artificially low thermal parameters, also for clarity of the drawing.

The anomalously large values of  $U_{22}$  for both Re and Si were initially interpreted as due to residual absorption effects or other possible systematic errors in the data. However the structural determination<sup>185</sup> of the isomorphous  $\text{Mn}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$  shed new light on this problem. The manganese compound crystallizes in the space group  $A2/m$  with cell dimensions,  $a = 11.788(2) \text{ \AA}$ ,  $b = 10.480(2) \text{ \AA}$ ,  $c = 13.744(2) \text{ \AA}$  and  $\beta = 117.367(6)^\circ$ . (This is identical to  $C2/m$  with the  $a$  and  $c$  axes interchanged). Here again the phenyl rings are disordered in the same



TABLE 50: ANISOTROPIC THERMAL PARAMETERS

FOR ORDERED MODEL

| Atom | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$ | $U_{13}$   | $U_{23}$ |
|------|------------|------------|------------|----------|------------|----------|
| Re   | 0.0291(3)  | 0.0534(3)  | 0.0357(3)  | 0        | 0.0167(2)  | 0        |
| Si   | 0.0314(13) | 0.0660(17) | 0.0364(13) | 0        | 0.0157(11) | 0        |

TABLE 51: POSITIONAL PARAMETERS AND ISOTROPIC B'S

FOR ORDERED MODEL

| Atom | x          | y           | z          | B        |
|------|------------|-------------|------------|----------|
| Re   | 0          | 0.14224(3)  | 0          | 3.06*    |
| Si   | 0.1388(2)  | 0           | 0.1678(2)  | 3.53*    |
| C1   | 0.0724(8)  | 0.1448(6)   | -0.1054(9) | 4.04(15) |
| C2   | 0.1041(5)  | 0.2649(7)   | 0.1069(6)  | 3.99(12) |
| O1   | 0.1162(7)  | 0.1518(5)   | -0.1686(8) | 6.09(16) |
| O2   | 0.1682(7)  | 0.3414(6)   | 0.1658(7)  | 6.03(15) |
| C11  | 0.1424(8)  | 0.0146(13)  | 0.3289(6)  | 3.1(2)   |
| C12  | 0.1265(10) | 0.1262(10)  | 0.3807(10) | 3.9(3)   |
| C13  | 0.1301(10) | 0.1237(10)  | 0.4987(10) | 4.9(4)   |
| C14  | 0.1496(8)  | 0.0097(13)  | 0.5649(6)  | 5.2(3)   |
| C15  | 0.1655(10) | -0.1018(10) | 0.5130(10) | 5.1(3)   |
| C16  | 0.1620(10) | -0.0994(10) | 0.3950(10) | 4.5(3)   |
| C21  | 0.2854(15) | 0.0165(13)  | 0.2008(34) | 3.5(2)   |
| C22  | 0.3172(22) | -0.0106(15) | 0.1090(19) | 3.9(2)   |
| C23  | 0.4261(29) | -0.0043(14) | 0.1382(21) | 4.7(2)   |
| C24  | 0.5033(15) | 0.0292(13)  | 0.2591(34) | 4.5(3)   |



Table 51 (con't)

| Atom | x           | y           | z           | B       |
|------|-------------|-------------|-------------|---------|
| C25  | 0.4715 (22) | 0.0563 (15) | 0.3509 (19) | 6.9 (4) |
| C26  | 0.3626 (29) | 0.0500 (14) | 0.3218 (21) | 4.6 (3) |

\*Equivalent isotropic temperature factor corresponding to the anisotropic thermal parameters shown in Table 50.

TABLE 52: SELECTED BOND LENGTHS AND ANGLES

(A) BOND LENGTHS ( $\text{\AA}$ )

|        |           |        |           |
|--------|-----------|--------|-----------|
| Re-Re  | 3.001 (1) | Re-Si  | 2.542 (3) |
| Re-Cl  | 1.95 (1)  | Re-C2  | 1.93 (1)  |
| Si-Cl1 | 1.92 (1)  | Si-C21 | 1.91 (1)  |
| Cl-O1  | 1.18 (1)  | C2-O2  | 1.17 (1)  |

## (B) ANGLES (DEGREES)

|                        |           |            |           |
|------------------------|-----------|------------|-----------|
| Re-Si-Re' <sup>a</sup> | 72.3 (1)  | Si-Re-Si'  | 107.7 (1) |
| Cl-Re-Cl'              | 178.4 (4) | C2-Re-C2'  | 95.6 (4)  |
| Cl-Re-C2               | 88.0 (3)  | Cl-Re-Si   | 95.1 (2)  |
| C2-Re-Si               | 78.7 (2)  | Cl1-Si-C21 | 105.0 (4) |
| Cl1-Si-Re              | 114.1 (3) | Cl1-Si-Re  | 117.6 (4) |
| Re-Cl-O1               | 177.2 (6) | Re-C2-O2   | 176.0 (7) |

<sup>a</sup>Primed atoms are related by either the mirror plane or the two-fold axis, whichever is applicable.





way as the rhenium analogue. In addition the anisotropic thermal parameters for the metals and the silicon atoms are similar in the two compounds. It therefore seems unlikely that the anomalous thermal parameters in both compounds are due to systematic errors in the data.

It was believed possible that the disorder, observed in the phenyl groups, where the data permit resolution of the disorder, could reflect a disorder of the whole molecule. A proper assessment of this possible disorder becomes important then, in order to obtain unambiguous bond lengths and angles.

The high anisotropy in the heavy atom vibrational ellipsoids observed in both the rhenium and manganese compounds provided the clue to the mode of disorder. Since the major axes of the thermal ellipsoids in both compounds were much larger than the other axes, it was believed that the disorder involved slight displacements of the molecule along the crystallographic *b* axis, as shown in Fig. 29. The vibrational ellipsoids are certainly large enough to contain two distinct rhenium and silicon populations, separated from their disorder averaged positions by approximately 0.15 Å.

Thus the completely disordered model was refined



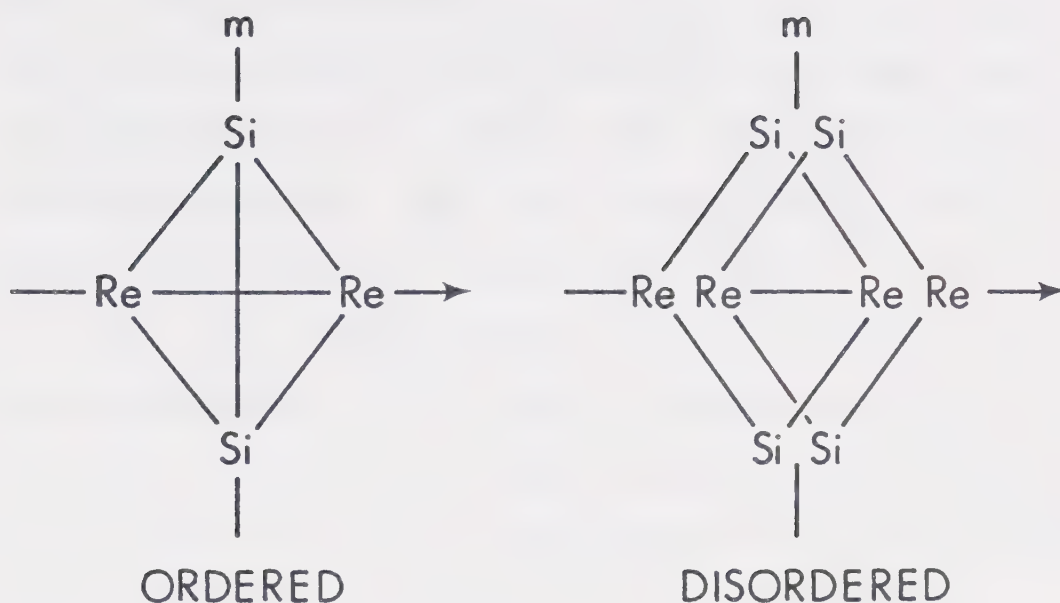


Fig. 29: Mode of Disorder in  $\text{Re}_2(\text{CO})_8[\text{Si}(\text{C}_6\text{H}_5)_2]_2$ .

to test whether it gave any better fit to the experimental data than the model involving an ordered  $\text{Re}_2\text{Si}_2$  cluster. In the least squares refinement the parameters for the rhenium and silicon atoms were refined without restriction, other than that imposed by symmetry. However all the parameters for the carbon and oxygen atoms of the carbonyl groups were not refined due to correlations between the  $x$  and  $z$  coordinates of the two disordered molecules. Thus for one of the disordered forms all coordinates were refined while for the other molecule only the  $y$  coordinate was refined. After a cycle of refinement



the x and z coordinates of the second molecule were set equal to those of its disorder-related mate and a further cycle was repeated with the same restrictions on the parameters. This was repeated until further iteration produced no significant shifts.

The final model had all atoms located at approximately  $0.3 \text{ \AA}$  from their disorder-related partners. Thus the data were of good enough quality to differentiate the two disordered molecules although only  $0.3 \text{ \AA}$  apart. The validity of the completely disordered model was verified by a Hamilton's R Test<sup>79</sup> at the 0.005 significance level, showing that the disordered model was significantly better than the ordered model. In the final least squares cycle  $R_1 = 0.035$  and  $R_2 = 0.056$  for 68 refined parameters. The anisotropic thermal parameters are shown in Table 53. The final positional parameters for all atoms in the completely disordered model are shown in Table 54 along with the isotropic B's of all atoms.

Electron density difference maps were also calculated for each model and were again found to be better for the completely disordered model with less residual electron density in its map. The highest peaks on each map were  $1.39e \text{ \AA}^{-3}$  and  $1.11e \text{ \AA}^{-3}$  for the ordered and disordered models respectively, this



TABLE 53: ANISOTROPIC THERMAL PARAMETERS FOR DISORDERED MODEL

| Atom <sup>a</sup> | U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>12</sub> | U <sub>13</sub> | U <sub>23</sub> |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Re                | 0.0274(6)       | 0.0215(17)      | 0.0353(6)       | 0               | 0.0157(4)       | 0               |
| Re'               | 0.0304(6)       | 0.0211(18)      | 0.0361(6)       | 0               | 0.0175(4)       | 0               |
| Si                | 0.0318(12)      | 0.021(7)        | 0.0370(12)      | 0.0000(12)      | 0.0158(11)      | 0.0000(13)      |

<sup>a</sup> Primed atoms are the disorder-related atoms.





TABLE 54: POSITIONAL PARAMETERS AND  
ISOTROPIC B'S FOR DISORDERED MODEL

| Atom | x <sup>a</sup> | y            | z            | B       |
|------|----------------|--------------|--------------|---------|
| Re   | 0.0            | 0.1578 (4)   | 0.0          | 2.18*   |
| Re'  | 0.0            | 0.1266 (3)   | 0.0          | 2.24*   |
| Si   | 0.1387 (2)     | 0.0178 (11)  | 0.1678 (3)   | 2.37*   |
| C1   | 0.0743 (11)    | 0.1594 (19)  | -0.1030 (13) | 3.3 (4) |
| C1'  | 0.0743         | 0.1303 (20)  | -0.1030      | 3.5 (5) |
| C2   | 0.1037 (10)    | 0.2773 (20)  | 0.1056 (11)  | 2.9 (5) |
| C2'  | 0.1037         | 0.2486 (20)  | 0.1056       | 3.8 (5) |
| O1   | 0.1169 (10)    | 0.1697 (16)  | -0.1672 (11) | 5.0 (4) |
| O1'  | 0.1169         | 0.1349 (16)  | -0.1672      | 5.1 (4) |
| O2   | 0.1674 (13)    | 0.3450 (17)  | 0.1639 (13)  | 4.0 (4) |
| O2'  | 0.1674         | 0.3308 (25)  | 0.1639       | 8.7 (6) |
| C11  | 0.1423 (8)     | 0.0146 (13)  | 0.3295 (6)   | 3.1 (2) |
| C12  | 0.1268 (10)    | 0.1254 (10)  | 0.3817 (10)  | 4.1 (3) |
| C13  | 0.1301 (10)    | 0.1224 (10)  | 0.4990 (10)  | 4.9 (4) |
| C14  | 0.1488 (8)     | 0.0086 (13)  | 0.5641 (6)   | 5.2 (2) |
| C15  | 0.1643 (10)    | -0.1022 (10) | 0.5119 (10)  | 5.3 (3) |
| C16  | 0.1610 (10)    | -0.0992 (10) | 0.3946 (10)  | 4.7 (3) |
| C21  | 0.2861 (26)    | 0.0167 (12)  | 0.2009 (33)  | 3.5 (2) |
| C22  | 0.3175 (22)    | -0.0094 (15) | 0.1092 (19)  | 3.9 (2) |
| C23  | 0.4259 (29)    | -0.0036 (14) | 0.1382 (21)  | 4.6 (2) |
| C24  | 0.5029 (16)    | 0.0283 (12)  | 0.2589 (33)  | 4.6 (3) |



Table 54 (con't)

| Atom | x           | y           | z           | B       |
|------|-------------|-------------|-------------|---------|
| C25  | 0.4715 (22) | 0.0544 (15) | 0.3505 (19) | 6.5 (4) |
| C26  | 0.3631 (29) | 0.0486 (14) | 0.3215 (21) | 4.4 (3) |

\*Equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 53.

<sup>a</sup>Where standard deviations are not given, the parameters were not refined.



density being located in the vicinity of the rhenium atoms in each map.

Thus although it seems that the data are best fitted using the disordered model, the initial ordered model (involving only disordered phenyl groups) is believed to provide a good description of the average geometry, and therefore bond lengths and angles obtained from this model are suitable. This is due to the mode of disorder which involves only a small translation of the whole molecule collinear with the Re-Re bond. The thermal parameters in this model cannot, however, be given any chemical significance since they (especially the  $U_{22}$ 's) reflect the disorder present. That the ordered model provides a good description of the average geometry of the molecule is also seen from the bond lengths and angles, which are all reasonable and in good agreement with the related molecules,  $\text{Re}_2(\text{CO})_8\text{H}_2\text{Si}(\text{C}_6\text{H}_5)_2$ ,<sup>65</sup>  
 $\text{Re}_2(\text{CO})_6\text{H}_4[\text{Si}(\text{C}_2\text{H}_5)_2]_2$  and  $\text{Re}_2(\text{CO})_7\text{H}_2[\text{Si}(\text{C}_2\text{H}_5)_2]_2$ .



APPENDIX 2: PROGRAMMES USED IN CRYSTAL  
STRUCTURE SOLUTION, REFINEMENT AND ANALYSIS

| AUTHOR                         | PROGRAMME           | DESCRIPTION                                                                                                                                                                                                 |
|--------------------------------|---------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| D. P. Shoemaker                | MIXG2               | Calculates Picker diffractometer settings from unit cell dimensions and cell type.                                                                                                                          |
| M. J. Bennett                  | PMMO                | Transforms raw data to intensities, applying $L_p$ corrections.                                                                                                                                             |
| M. Elder and<br>K. A. Simpson  | D-REFINE            | Refines cell parameters for all space groups.                                                                                                                                                               |
| A. Zalkin                      | FORDAP              | Fourier summation for Patterson or Fourier maps.                                                                                                                                                            |
| W. C. Hamilton                 | GON09 <sup>a</sup>  | Absorption corrections for Picker data.                                                                                                                                                                     |
| P. Coppens                     | DATAP <sup>b</sup>  | Absorption and Extinction corrections.                                                                                                                                                                      |
| C. T. Prewitt                  | SFLS5               | Structure factor calculation and least squares refinement of parameters. Modified by B. M. Foxman and M. J. Bennett for rigid body routine, and by W. L. Hutcheon and M. J. Bennett for the hindered rotor. |
| J. S. Woods                    | MGEOM <sup>a</sup>  | Calculates bond lengths, angles and best planes.                                                                                                                                                            |
| M. E. Pippy and<br>F. R. Ahmed | NRC-22 <sup>b</sup> | Calculates least squares planes.                                                                                                                                                                            |
| W. Busing and<br>H. A. Levy    | ORFFE               | Calculates bond lengths, angles, and associated standard deviations; modified by B. Penfold for I.B.M. 360 and W. L. Brooks and M. Elder for hindered rotors and rigid bodies.                              |





| AUTHOR                                  | PROGRAMME | DESCRIPTION                                                                                                                                                                  |
|-----------------------------------------|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| C. Johnson                              | ORTEP     | Writes Plot Command for Calcomp plotter, for plotting three dimensional molecular representations. Calculates bond lengths and principal axes of anisotropic thermal motion. |
| M. J. Bennett<br>and B. M. Foxman       | MMMR      | Calculates starting parameters for rigid bodies and hindered rotors.                                                                                                         |
| M. Cowie                                | PUBE      | Sorts data according to any desired sequence of h, k, or l.                                                                                                                  |
| R. C. Elder                             | PUBTAB    | Prints Structure Factor Amplitude Tables; modified by M. Cowie to work in conjunction with PUBE.                                                                             |
| G. J. B. Williams<br>FRAME <sup>c</sup> |           | Converts continuous paper tape output from automatic diffractometer, in ASCII code to "framed" output on cards in EBCDIC coding, suitable for PMMO input.                    |

<sup>a</sup>This programme was used for the two rhenium hydrides.

<sup>b</sup>This programme was used for the three tris dithiolene complexes.

<sup>c</sup>This programme was used only for  $[\text{Ph}_4\text{As}][\text{Nb}(\text{bdt})_3]$ . In the other two structures collected by automatic diffractometer, magnetic tape output was used. This was translated from ASCII by a subroutine added to PMMO by myself.















**B30086**